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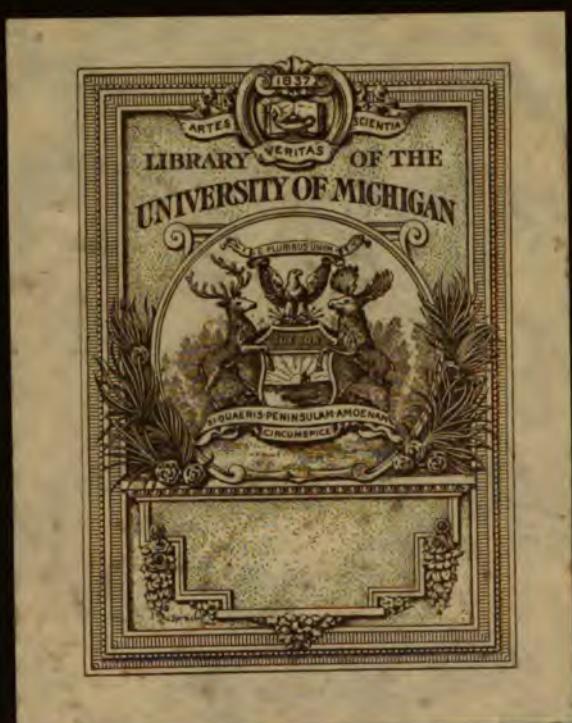
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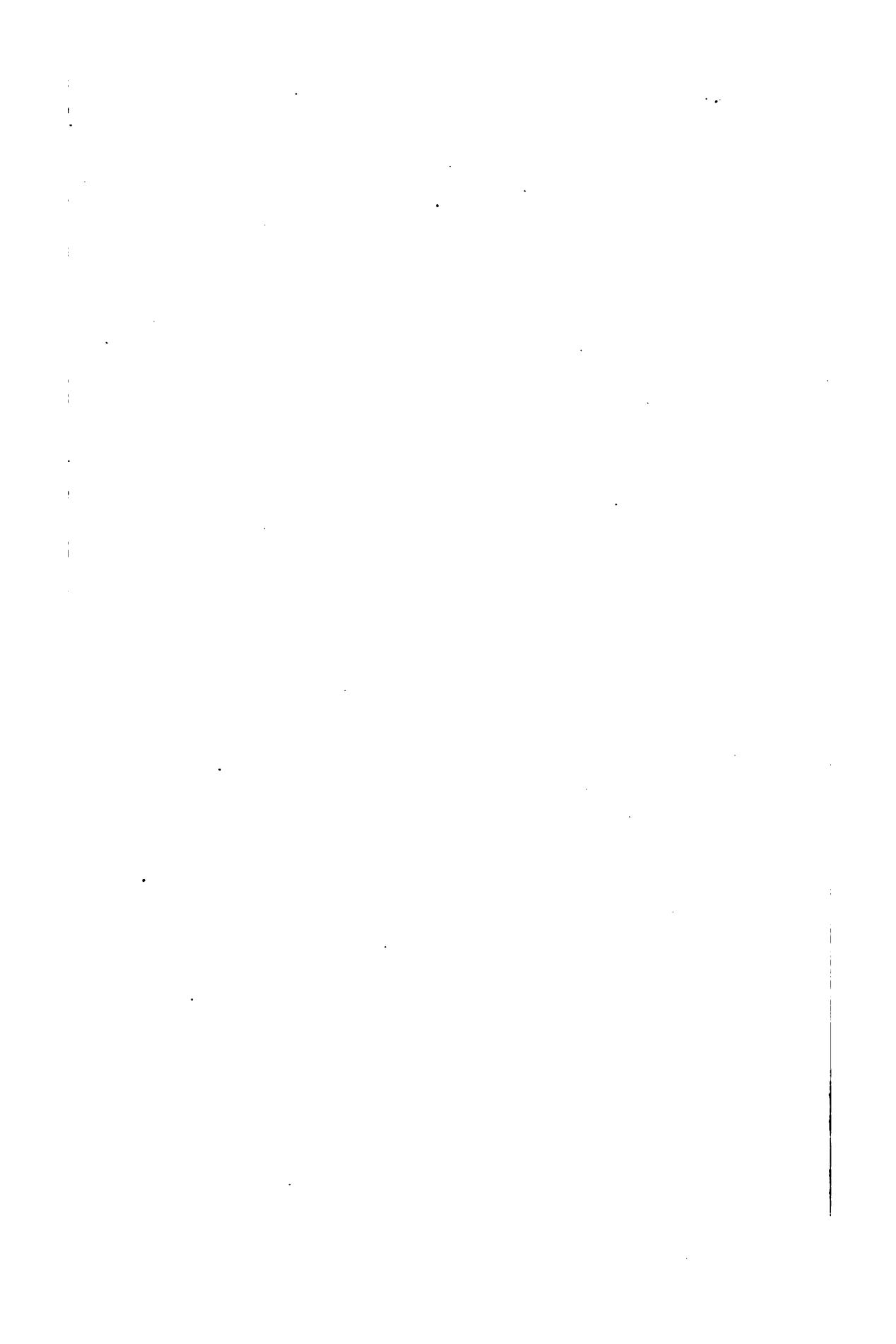
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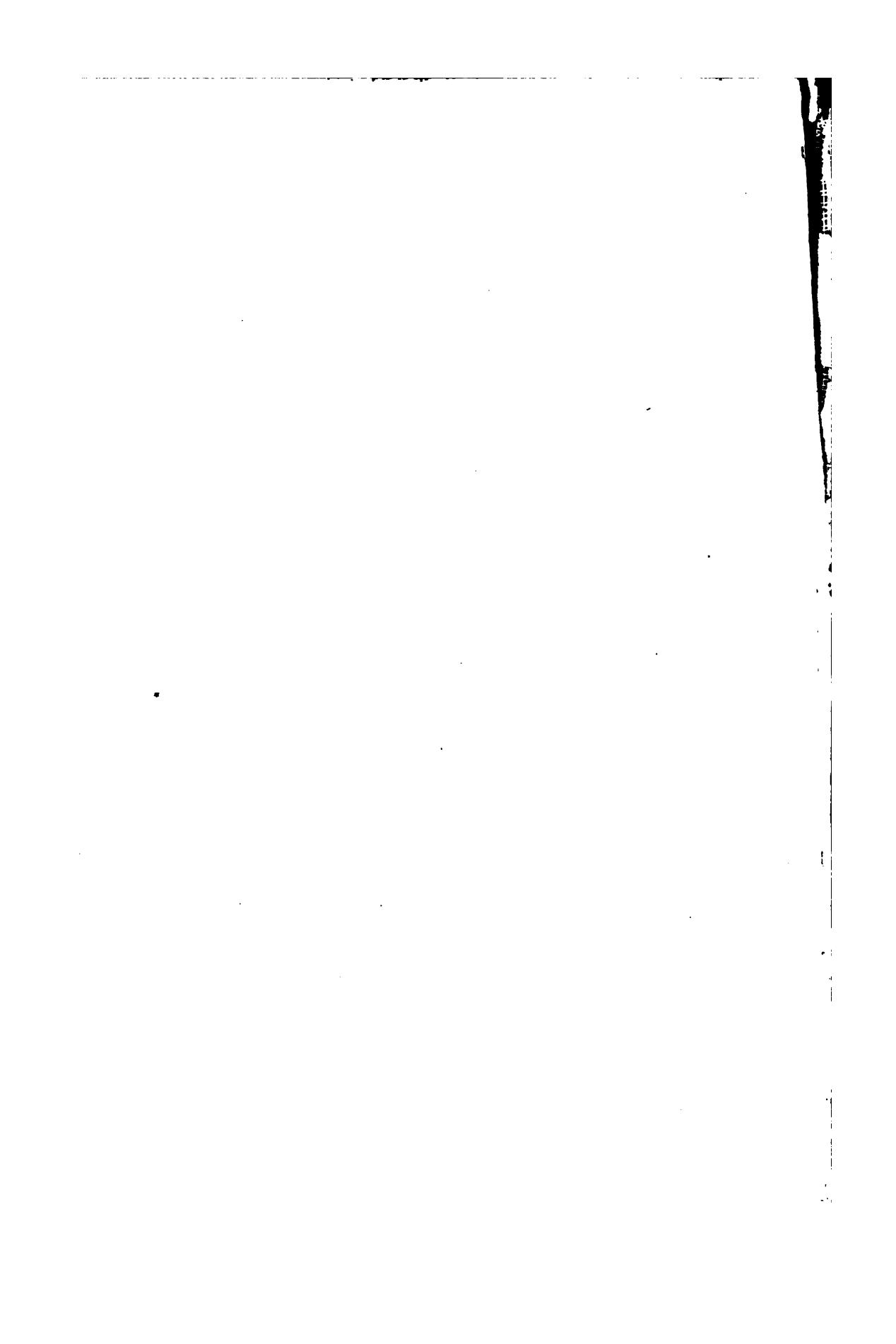
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RAPID METHODS  
FOR THE  
**CHEMICAL ANALYSIS**  
OF  
SPECIAL STEELS, STEEL-MAKING  
ALLOYS, AND GRAPHITE

BY  
**CHARLES MORRIS JOHNSON, PH.M.**  
CHIEF CHEMIST TO THE PARK STEEL WORKS OF THE CRUCIBLE  
STEEL COMPANY OF AMERICA

*SECOND EDITION, REWRITTEN*  
FIRST THOUSAND

NEW YORK  
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1914

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BY

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Stanhope Press

F. H. GILSON COMPANY  
BOSTON, U.S.A.

## PREFACE.

IN offering this little volume the author desires to call attention to the portions of it that he has worked out in his own way and that are, as far as he is aware, new features. (1) A qualitative test for titanium in the *presence* of vanadium. (2) The annealed test for chromium in steel. (3) The test for annealing in steel. (4) The pouring of the indicator into the solution when titrating for vanadium and chromium in steel, in the presence of either or both elements. (5) The determination of small amounts of copper and nickel in steel and ferro-vanadium by first separating the copper and nickel from the bulk of the iron and vanadium by means of potassium ferricyanide. (6) The EXACT determination of phosphorus in ferro-vanadium, demonstrating that as little as one-eighth of the actual phosphorus may be obtained by the ordinary processes. (7) The application of the new heating wire to a combustion tube. (8) The modified method for higher per cents of nickel. (9) The determination of silicon carbide in old plumbago crucibles and ITS EXISTENCE THEREIN. (10) The automatic laboratory still. (11) The simple laboratory method for making clay combustion boats. (12) The method for annealing Hadfield's steel. (13) The method for the rapid volumetric determination of manganese in the presence of iron, calcium and magnesium, by means of potassium ferricyanide. (14) The new form of potash absorption and weighing apparatus for carbon dioxide. (15) The new form of combustion train.

The test for annealing in steel was first suggested to the writer about ten or twelve years ago by Dr. E. S. Johnson. The author has since studied it in its application to all kinds of alloy steels.

It is the author's hope that, at least, some of the information contained in this book may prove as helpful to its readers as it has to him.

PITTSBURGH, PA., July 1, 1908.



## INTRODUCTION TO THE SECOND EDITION.

The author wishes: *1st.* — To devote the preface of the second edition of his book to emphasizing the generalization, or rule which he believes should guide those who wish to experiment in the alloying of iron with other elements: The general statement can be expressed as follows: If iron be combined by fusion with notable quantities of an element whose melting point is very much below that of iron, the tendency is to produce a metal of inferior physical properties, but if iron be combined with an element whose melting point is nearly that or higher than that of iron, then the tendency is to produce a metal of superior physical properties.

It would seem safe to add that the lower the melting point of the non-ferrous element, the more inferior the resultant metal and the higher the melting point of the non-ferrous constituent, the more valuable the properties of the resulting metal.

The common enemies of steel are phosphorus (m. p.  $44^{\circ}$  C.) and sulphur (m. p.  $114$  to  $120$ ° C.) Much has been written about the evil effects of nitrogen in steel; with a melting point of  $-214$ ° C., this is to be expected. Tin alloys readily with iron and the writer knows from his own experiments that  $0.400$  per cent of tin causes in steel both cold and red shortness. Its melting point is  $232$ ° C. Lead (m. p.  $326$ ° C.), bismuth (m. p.  $270$ ° C.) and cadmium (m. p.  $321$ ° C.) are to be feared as much as tin. Arsenic (m. p.  $480$ ° C. under pressure), zinc (m. p.  $419$ ° C.), antimony ( $630$ ° C.) and aluminum ( $658$ ° C.) cannot be expected to produce desirable alloys with iron. Copper, whose melting point ( $1083$ ° C.) is  $437$ ° C. below the melting point of iron ( $1520$ ° C.) causes notable red shortness when present to the extent of  $1$  per cent and less, depending on the amount of carbon, etc., present.

The beneficial results of alloying iron with elements near its own melting point, such as chromium ( $1505^{\circ}$  C.), nickel ( $1450^{\circ}$  C.), cobalt ( $1490^{\circ}$  C.), are matters of everyday metallurgical knowledge. Vanadium with a still higher melting point, around  $1700^{\circ}$  C., is famous for its useful combinations with iron in conjunction with chromium or tungsten, or both. Great claims are made for the beneficial effect of combining titanium with iron but, as yet, in quantities of less than 1 per cent. The author ventures the prediction, that this element will be combined with iron in greater quantities producing results that will justify the expense.\* Advancing still higher in the scale of melting point, molybdenum stands out as an element that has been alloyed with iron in notable quantities with splendid results but its high price has caused its replacement by the cheaper element, tungsten whose still higher melting point of  $3000^{\circ}$  C. makes it the logical superior of molybdenum with a melting point approximating  $2500^{\circ}$  C.

Last of all we come to carbon which does not melt at all but finally succumbs to the temperature of the electric arc, by volatilizing around  $3500^{\circ}$  C. This most wonderful of all of the elements can be truly styled the exponent and intensifier of all the virtues that steel possesses.

*2nd.* — Attention is directed to the author's method for the determination of phosphorus in tungsten bearing materials.

*3rd.* — To his method for the determination of tungsten in its ores.

*4th.* — To his method for the determination of sulphur in alloy steels by heating the insoluble carbides, which carry the major part of the sulphur, to a yellow heat in a stream of acid — carrying hydrogen, evolving the sulphur from sulphates such as barium sulphate in the same manner, as hydrogen sulphide.

*5th.* — To his modification of Brunck's method for nickel in steel.

\* The experimenter should insist on alloys that are free from low melting elements such as aluminum or any of the above; as free as at all possible, or otherwise he may condemn the high melting elements for the shortcomings of low ones that he has added unawares.

*6th.* — To his method for the titration of iron or vanadium, or both, in the presence of uranium, getting the latter by difference, all in the one operation, after having weighed all as total oxides.

*7th.* — To his method for the determination of uranium in ores, in ferro-uranium and in steels.

*8th.* — To the complete methods for the analysis of cobalt steels and cobalt metals.

*9th.* — To the author's investigation of the cause of bark in pipe-annealed steel.

*10th.* — To his tapered clay combustion tube, eliminating all rubber stoppers.

*11th.* — To his milling machine, one piece nichrome triangle and the plan and views of the laboratory rooms.

*12th.* — The second edition contains 200 pages of additional material.

*13th.* — The author wishes to thank all of those who have made the second edition of this book possible by investing in the first edition.

He has endeavored to bring his book up to the latest and best analytical practice in iron, steel and its alloys. He has added chapters on the testing of lubricating oils, coal, iron ores, fluorspar, limestone, sand and fire-brick to save some of his younger readers the time he has spent in wading through the maze of literature on some of these topics, especially the first one.

PITTSBURGH, PA., Oct. 10, 1913.



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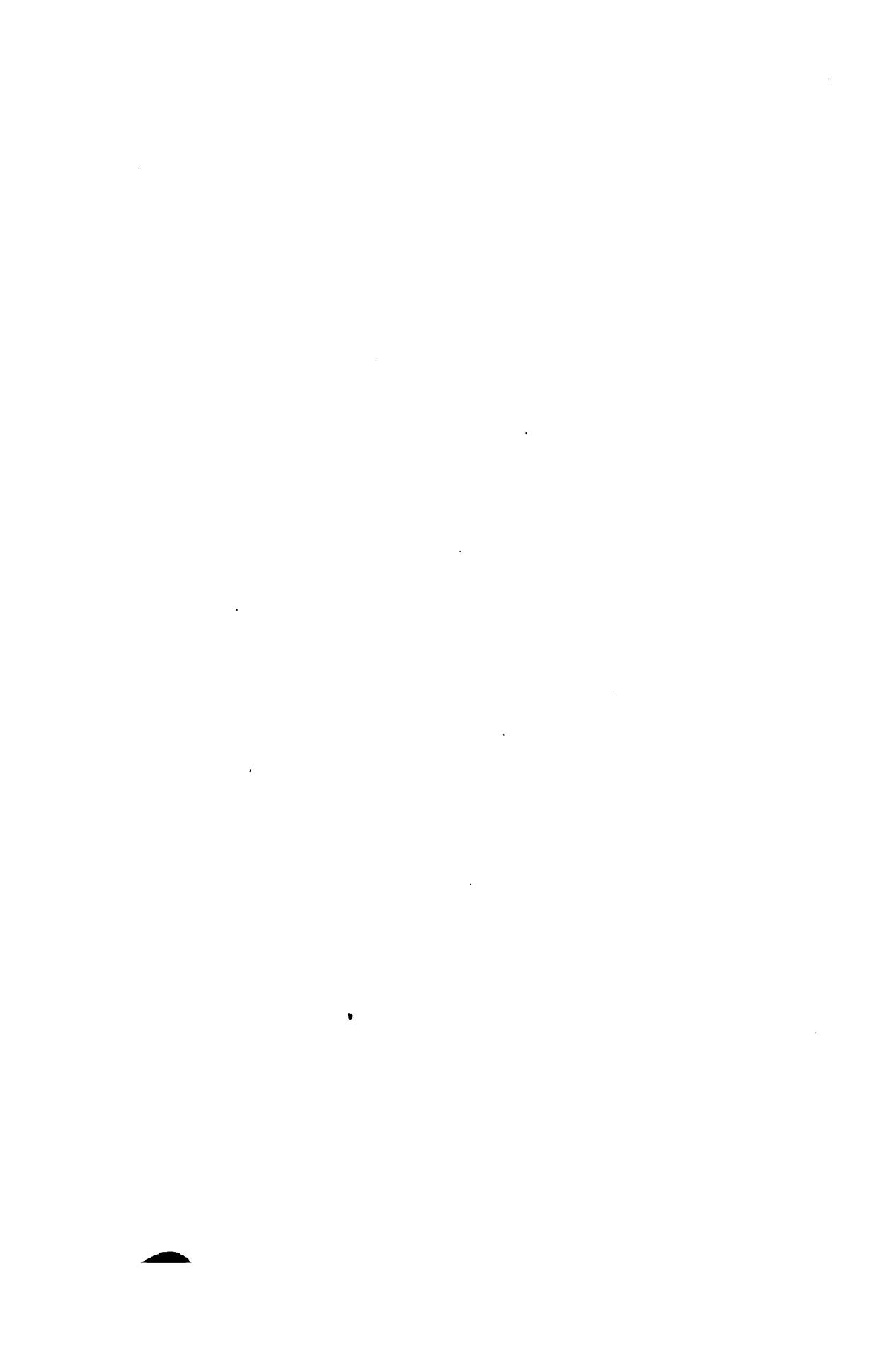
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## **ANALYSIS OF SPECIAL STEELS, STEEL-MAKING ALLOYS AND GRAPHITE.**

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### **CHAPTER I.**

#### **QUALITATIVE TESTS FOR CHROMIUM, TUNGSTEN, NICKEL, MOLYBDENUM, ETC.**

**DISSOLVE** 0.200 gram of the sample with 5 c.c. 1 : 3 sulphuric acid in 152.4 (6 inches) by 16 mm. test tube. Also 0.200 gram of a plain carbon steel in the same way. Place the two tests in boiling water for a half hour.

The plain carbon steel will be free from black sediment and practically water white as to color. If the unknown contains as little as 0.2 or 0.3 per cent of chromium it will look distinctly greener than the known steel. Nickel also produces this effect, but the color is not so marked.

If the steel has 0.100 to 0.3 per cent of tungsten a black insoluble residue will be found in the bottom of the tube. This black sediment forms also with similar amounts of molybdenum and phosphorus. But on addition of 1 c.c. of 1.20 nitric acid to such a solution the black entirely disappears if due to the presence of the two last named elements. The black precipitate, if caused by a small quantity of tungsten, on addition of the nitric acid, changes to a yellow one. If the amount of the latter is small it is better to put the test tube back on the water bath and permit the tungstic acid to settle for two hours, when it can be seen plainly as a yellow spiral thread rising up through the solution by giving the test tube a rotary motion. The black residue of phosphide can be recognized by filtering it out and dropping 1 : 1 hydrochloric acid on it, when the characteristic odor of phosphine is obtained. Or it can be

dissolved off the filter with 1.20 nitric acid and the filtrate precipitated with molybdate solution after boiling it with a slight excess of potassium permanganate. Finish as in plain steel to get the yellow precipitate. If steels are quite high in silicon, the silicic acid and the carbon, together, produce black flakes that float about. They turn to white ones on being heated with 1.20 nitric acid on a water bath for an hour or two.

The annealed test for chromium is given under "Annealing of Steel." (See page 345.)

#### MOLYBDENUM.

A further qualitative test for the latter element is as follows: Dissolve 0.500 gram of sample in 25 c.c. of 1 : 1 hydrochloric acid. Boil till action ceases, using a 254 by 25.4 mm. (10 by 1 inch) tube. Heat further with 2.5 grams of potassium chlorate until a clear solution has been obtained or the residue, if any, is a bright yellow. Add an equal volume of water. Filter without washing. Dissolve 10 grams of potassium hydroxide in 10 c.c. of water. Add this to the filtered solution. Boil for five minutes. Filter. Do not wash. Pour 8 c.c. of this filtrate into a 254 by 25.4 mm. tube. Add conc. hydrochloric acid until crystals form. Dilute with water to 30 c.c. Add a few grains of granulated tin. Heat to the first indication of boiling; remove from heat immediately and cool. Add to the cold solution 2 c.c. of potassium sulphocyanate. A light brownish red indicates 0.2 or 0.3 per cent of molybdenum. A distinct red indicates 1 to 2 per cent and a deep red higher amounts of molybdenum. This is a fine test, but if the mistake is made of boiling the solution too long with the tin scarcely any color is obtained. Bring, therefore, to incipient boiling, only, after putting in the grains of tin. Then remove at once from the fire and test with the KCNS as already described. For *nickel* the quantitative analysis as given on page 164 is so rapidly carried out that it constitutes an easy qualitative test also.

For qualitative tests for titanium and vanadium see page 4.

## QUALITATIVE TESTS FOR CHROMIUM, TUNGSTEN, ETC. 3

For qualitative tests for copper in steel see page 151. For qualitative tests for copper in ferro-vanadium see page 154. For qualitative test for nickel in steel see, also, page 10.

Qualitative test for cobalt: (See page 303.)

Qualitative test for nickel: Dissolve 0.5 gram of the steel as given for vanadium on page 4. When the red fumes are gone cool; add 2 grams of citric acid and then ammonia until the solution is ammoniacal and clear. Now introduce a solution of dimethylglyoxime of the strength given on page 176. A scarlet precipitate will form if nickel is present. See also page 303 if the chemist wishes to first remove the iron before adding the "dimethyl" which is a better way if the per cent of nickel is very small.

Qualitative test for titanium in the presence of vanadium: Dissolve the steel as for vanadium as given on page 4 but in a small boiling flask, using 0.5 gram of sample. Then peroxidize as described on page 23 taking proportionately smaller amounts of the sodium peroxide and carbonate. Redissolve the iron hydroxide, after washing it with peroxide water, and peroxidize again, and so on until some of the filtrate from the iron hydroxide no longer gives a vanadium test with  $H_2O_2$  on being boiled down to one-half with twice its bulk of conc. nitric acid. The iron hydroxide can then be dissolved with 1.20 nitric acid and be tested with hydrogen peroxide for Ti. The iron hydroxide will contain all of the Ti, free from V.

## CHAPTER II.

### \* ANALYSIS OF VANADIUM STEEL AND FERRO-VANADIUM.

THE determination of vanadium in the presence of tungsten, titanium, chromium, nickel, manganese, silicon, molybdenum, copper and aluminum has been studied by the author. It has been the latter's aim to produce modified methods that combine speed, simplicity and accuracy. The underlying reactions are well known and have been variously applied by different chemists.

#### QUALITATIVE TESTS.

##### *Absence of Titanium.*

A qualitative test for vanadium can be completed in a half hour or less, even in the presence of 4 per cent of chromium, although there be but 0.05 per cent of vanadium in solution. Dissolve 0.500 gram of steel in a 254 by 25.4 mm. test tube (10 by 1 inch) in 10 c.c. 1 : 3 sulphuric acid, heating until action ceases, adding a little water, if necessary, to dissolve any sulphate of iron that may separate during the boiling. 5 c.c. of concentrated nitric acid are used to oxidize the iron and hypo-vanadic acid. Heating is continued until red fumes disappear. If tungsten be present, filter through paper. Filter without washing. Pour some of the filtered or unfiltered fluid, as the case may be, into two 152 by 16 mm. test tubes, allowing about 5 c.c. of the solution to each tube. To one of these portions add 5 c.c. of sodium peroxide dissolved in dilute sulphuric acid. To the other add 5 c.c. of water. The portion to which the sodium peroxide was added assumes a reddish brown shade if vanadium is present.

\* From a paper read before the Pittsburgh section of the American Chemical Soc., Jan. 23, 1908.

If there be enough chromium to give the solution a dark green tint, then hold the tubes against an illuminated white shade. The vanadic solution containing peroxide will plainly show a browner tint than its mate, to which no peroxide was added. The white shade greatly lessens the interference of the chrome green. The peroxide is prepared by dissolving 3.5 grams of sodium peroxide in 125 c.c. of 1 : 3 sulphuric acid and diluting with distilled water to 500 c.c. Add the water last, when preparing the peroxide solution.

#### QUALITATIVE TEST FOR VANADIUM IN THE PRESENCE OF TITANIUM.

Recent works on steel analysis give the peroxide qualitative test for vanadium and titanium but dismiss the subject with comment that either element interferes with the qualitative test for the other. The writer has overcome this interference by the use of ferrous ammonium sulphate which, as far as he is aware, is a new departure. By this means as little as 0.100 per cent of titanium can be detected without the least difficulty in the presence of ten times as much vanadium, in spite of the fact that the color of vanadium with peroxide is much stronger than that of titanium and hydrogen peroxide. The principle involved is, briefly, that ferrous ammonium sulphate discharges the brick red color obtained by mixing a vanadic solution with hydrogen peroxide more quickly than it does the yellow shade of the titanic acid and H<sub>2</sub>O<sub>2</sub>. An extract from the author's experimental records illustrates the procedure. The regular ferrous ammonium sulphate standard as given for vanadium titrations, later in this chapter, was used for the experiments (A) and (B) and other similar ones.

Experiment A was repeated with gradual increase of vanadium up to 1 per cent V, keeping the titanium still at 0.13 per cent, with results identical with the above, so that even with ten times as much vanadium the latter was decolorized more quickly, and was slower in regaining color, when peroxide was again added, than the titanium.

## EXPERIMENT A.

	Reagent.	Result.
Mixture No. 1. $\left\{ \begin{array}{l} 500 \text{ mg. plain carbon steel, } 8 \text{ mg. } 8\% \text{ Ferro Ti, } 10 \text{ mg. of } 21.8\% \text{ Ferro V, or } 0.13\% \text{ Ti and } 0.436\% \text{ V.} \end{array} \right.$	1st, added 5 c.c. $H_2O_2$ solution. 2d, added 5 c.c. ferrous sulphate. 3d, added 5 c.c. more of sulphate. 4th, added 5 c.c. of $H_2O_2$ again.	Brick red color. Faded to distinct yellow. Decolorized. Return of distinct yellow.
Mixture No. 2. $\left\{ \begin{array}{l} 500 \text{ mg. plain carbon steel, } 10 \text{ mg. of } 22.0\% \text{ Ferro V, or } 0.44\% \text{ V. No Ti added.} \end{array} \right.$	1st, same as above. 2d, as in 2d No. 1. 3d, as in 3d No. 1. 4th, as in 4th No. 1.	Brick red color. Brick red nearly all gone. Brick red all gone. No return of red color until 10 minutes had elapsed.

A mixture containing 1 per cent V with 0.500 gm. plain steel behaved in the same manner as given in B. Vanadium gradually regains its red. A glance at the tabulation shows that, if the chemist wishes to detect titanium in the presence of vanadium, he need only resort to the simple expedient of adding slowly, a c.c. at a time, the ferrous ammonium sulphate standard to the qualitative vanadium test. If it gradually fades from a brick red to a bright yellow then titanium is surely present. But if the red or brown tint fades directly to a nearly colorless condition without showing a clear bright yellow then, at least, not more than a trace of titanium is present.

To render the qualitative tests decisive one should proceed exactly as outlined in the table as to amounts of peroxide and sulphate added. Under the conditions given the tests are very satisfactory.

Further, the color of plain vanadium steel with hydrogen peroxide is different from that obtained in like manner with titanium. Much vanadium (0.40 per cent) gives a strong brick red. Small amounts yield a brown. Titanium color with hydrogen peroxide is always a clear yellow unless vanadium is present.

## ANALYSIS OF VANADIUM STEEL AND FERRO-VANADIUM 7

## EXPERIMENT B.

	Reagent.	Result.
Mixture No. 1. $\left\{ \begin{array}{l} 500 \text{ mg. plain steel, } 8 \\ \text{mg. } 8\% \text{ Ferro Ti, or} \\ 0.13\% \text{ Ti.} \end{array} \right.$	1st, added 5 c.c. H <sub>2</sub> O <sub>2</sub> . 2d, added 5 c.c. sulphate. 3d, added 1 c.c. more of sulphate. 4th, added 1 c.c. more of sulphate. 5th, added 1 c.c. more of sulphate. 6th, added 1 c.c. more of sulphate. 7th, added 1 c.c. more of sulphate. 8th, added 1 c.c. more of sulphate. 9th, added 1 c.c. more of sulphate. 10th, added 1 c.c. more of sulphate. 11th, added 1 c.c. more of sulphate. 12th, added 1 c.c. of peroxide.	Distinct yellow. Do. Do. Do. Do. Do. Do. Yellow color less distinct. Yellow color fainter. Yellow color fainter. Yellow color all gone. Yellow color very strong.
Mixture No. 2. $\left\{ \begin{array}{l} 500 \text{ mg. plain steel, } \\ 10 \text{ mg. } 22.5\% \text{ Ferro} \\ V, \text{ or } 0.44\% \text{ V.} \end{array} \right.$	1st, added 5 c.c. H <sub>2</sub> O <sub>2</sub> . 2d, added 5 c.c. sulphate. 3d, added 1 c.c. more sulphate. 4th, same as above in 4th to 12th, No. 1. 12th, same as above in No. 1. 13th, added 1 c.c. more of peroxide. 14th, added 1 c.c. more of peroxide.	Strong brick red color. Red color nearly gone. Red color all gone. Red color all gone. Red color all gone. Slight return of brown. Faint coffee color.

The *quantitative* determination of vanadium and chromium\* in most varieties of vanadium steel can be made in a compara-

\* For very small amounts of Cr.—less than 0.100 per cent for example—take 10 to 40 grams of the steel and proceed by removing the bulk of the iron by BaCO<sub>3</sub> as given on page 146. Use the ash as directed in the footnote on page 146; add the solution of the fusion of the ash to the main Cr; convert to nitrate and finish for Cr as usual.

tively simple way. The writer proceeds as follows: Two grams of steel are heated in a mixture of 30 c.c. of 1 : 3 sulphuric acid and 20 c.c. of water in a 600 c.c. beaker. When the first action is over, 60 c.c. of 1.20 nitric acid are used to complete the solution and oxidize the iron. Boiling is continued two minutes longer and then 200 c.c. of water are introduced. From a small pipette a solution of permanganate of potassium is delivered, a little at a time, until a slight precipitate of manganese oxide is obtained that does not perceptibly dissolve after twenty minutes boiling. The beaker is removed from the fire and, after a few moments, is placed in a tray of water. Its contents are filtered into a heavy suction flask through an asbestos filter using a 1½-inch carbon filter tube, supporting the asbestos on a perforated porcelain plate.\* (The asbestos is washed in nitro-hydrochloric acid and freed from chlorine test with distilled water before it is used.) The residue on the asbestos filter is washed fifteen times with 20 c.c. of 1 : 3 sulphuric acid diluted with 500 c.c. of water.

The filtrate and washings are returned to the 600 c.c. beaker together with 30 c.c. of dilute sulphuric acid, additional. The volume is now about 350 c.c. and titration is begun with a standard of double sulphate of iron and ammonia. The double sulphate standard is dropped in from a 100 c.c. burette until the fluid in the beaker loses all brown tints and assumes a practically colorless shade, in plain vanadium, or in vanadium steels containing less than 1 per cent of chromium. If much chromium is present, i.e., from 2 to 6 per cent, the iron sulphate is added until the chrome green no longer grows darker, and two or three c.c. more to insure an excess. There are two reasons why the sulphate standard should be added at the start. In the first place, though no chromium may have been added to

\* Now use an alundum porous thimble 1 $\frac{1}{2}$  inches outside diameter and 2 inches high, supported in a glass filter tube 1 $\frac{1}{2}$  inches O. D. by 3 $\frac{1}{2}$  inches high. A piece of flat Gooch rubber tubing of 1 $\frac{1}{2}$ -inch diameter is required to make the tight connection between the thimble and the glass filter tube. This arrangement does away with the use of an asbestos filter and requires very little water pressure for rapid filtration. The apparatus is shown in the photo on page 247.

the steel, there is often a little manganic oxide held in solution, or permanganate, which would reduce a portion of the sulphate standard. Again there is never any certainty that small amounts of chromium are not present. The quantity of sulphate standard required in the foregoing reduction should be noted in case the determination of chromium is part of the program. The permanganate of potassium standard is next dropped into the solution and, as soon as the pink color begins to disappear slowly, the standard is added three drops at a time, until a very faint pink color is obtained that persists after 30 seconds stirring. Should even as much as five or six per cent of chromium be present a practiced eye can easily detect pink reflections through the chrome green. These pink glints can be seen in the bottom of the beaker and, as one looks down through the mouth of the latter, a rounded bright spot is seen that takes on a pink flush when the permanganate is in excess.

The solution is now ready for the titration of the vanadium, alone:<sup>\*</sup> 0.6 c.c. of potassium ferricyanide is poured into the beaker with a convenient dropper, having an etched mark on it to indicate the 0.6 c.c., so that the same quantity of the indicator is always taken.<sup>†</sup> The ferricyanide imparts a brown tint to the iron solution. The ferrous ammonium sulphate standard is again dropped in, a little at a time, until one drop produces a green coloration that is *free* from yellow tints.<sup>‡</sup> The titration is continued to a blue. The number of c.c. of double sulphate standard required in this second titration less the number needed to produce a similar shade in an imitation test, made with a steel that does not contain vanadium, gives the amount of the sulphate standard required to reduce the vanadic acid present. This remainder is multiplied by 2.54 to obtain the number of milligrams of vanadium in the sample. With each lot of analyses, two tests are made of plain steels to which

\* Read pages 39 to 42.

† 5 grams of potassium ferricyanide dissolved in 130 c.c. of water.

‡ Titrations are now all carried to a blue; i.e., until 3 drops of the double sulphate change the dark green to a distinct blue.

have been added known weights of standard ferro-vanadium drillings or powder. If the usual operations recover the vanadium added all of the tests made at the time are accepted. The amount of double sulphate standard required by the blank tests on non-vanadium steels is deducted from all tests before making calculations. This deduction for plain vanadium or vanadium-chrome steels where the per cent of chromium is not much in excess of three per cent, varies from 0.4 to 0.9 c.c. This applies to a volume of approximately 350 c.c. An increased volume produces an increased blank. A test, in duplicate, for vanadium by the foregoing manipulations can be carried through in an hour and a half in the presence of chromium, nickel, tungsten or molybdenum.

The presence of much chromium increases the blank somewhat. With no chromium present the blank is about 0.3 to 0.4 c.c. and, with chromium in the solution to the extent of 3 per cent, it is 0.7 to 0.9 c.c. With a chromium content of 4 per cent it is 1.0 to 1.2 c.c. It is always best to make control tests and blank tests, when high chromium and tungsten steels are being analyzed, with mixtures imitating closely the samples submitted for analysis. It is very important when dealing with alloy steels, containing large percentages of chromium and tungsten, to digest the drillings until the tungstic acid is a bright yellow before boiling with the excess of permanganate solution. One should, when the tungsten has "cleaned well," add permanganate until, after 20 minutes boiling, sufficient excess of manganese oxide is present to give the separated tungstic acid a chocolate color. Then proceed as usual.

When nickel is present in the steel in quantities ranging from 3 to 5 per cent the same method applies, but it must be borne in mind that, when ferricyanide of this concentration (5 grams in 130 c.c. of water) is used, in a few minutes, nickel ferricyanide separates, hence the titration must be proceeded with immediately.

Molybdenum does not interfere with the titration of vanadium, though the former element be present in large quantities.

## ANALYSIS OF VANADIUM STEEL AND FERRO-VANADIUM 11

\* The determination of vanadium in ferro-vanadiums of the low silicon type offers no difficulties except that segregation is considerable. It is always advisable to make at least three tests of each sample and average the results. From 0.3 to 0.6 gram are taken and proceeded with exactly as in steels until the titration is to be made when, instead of adding the double sulphate standard first, the completeness of the oxidation of the ferro-vanadium is tested by adding three drops of the permanganate standard. If this gives a suggestion of pink to the solution, the ferricyanide indicator is added and then the ferrous sulphate standard until the light sky blue of the vanadyl salt is darkened *slightly* by the deeper blue caused by the excess of ferrous standard. This end point is very satisfactory but requires a little experience on the part of the analyst. The amount of sulphate standard used is noted and then the permanganate standard is added, *at once*, until a *distinct* reddish pink color is obtained that does not fade perceptibly after thirty seconds vigorous stirring. This end point might be described as an old rose shade. Blanks are run on the same weights of a plain carbon steel in exactly the same way and deducted from the amount of sulphate required to produce the blue and from the amount of permanganate required to restore a pink color. If less permanganate than sulphate is used, after correcting the sulphate reading to the permanganate basis, the presence of chromium is indicated and a qualitative test for the latter element can be made in an hour by fusing 0.8 gram of the ferro-vanadium with 10 grams of sodium carbonate mixed with 2 grams of nitrate of potassium. The melt is dissolved in water. The residue is removed by filtration in the cold. A yellow tinted filtrate confirms the presence of chromium. Several tenths of 1 per cent of chromium are frequently present.

The amount of double sulphate should not be taken as a basis of percentage calculations unless it is positively known that chromium is absent. The sulphate should be first added as described. This should be immediately followed by the

\* Read pages 35 to 37.

addition of the permanganate standard as given and the amount of the latter standard required to produce the permanent reddish pink should be multiplied by 25.4 to find the milligrams of vanadium in solution. For instance in 50 per cent ferro-vanadium it is not practical to take more than 0.4 gram for analysis. One c.c. of the double sulphate equals 0.00086 gram of chromium or only 0.215 per cent chromium, but it also equals 0.635 per cent vanadium, i.e., 0.2 per cent chromium would raise the vanadium content 0.6 per cent if not eliminated by calculating the vanadium from the permanganate used to obtain the old rose tint. When ferro-vanadium contains much silicon, about 4 per cent or more, the borings or powder may not dissolve completely in sulphuric and nitric acids. The following modification is necessary: Treat 0.3 to 0.6 gram of sample with 60 c.c. 1.20 nitric acid in a No. 5 porcelain evaporating dish. When heat produces no further action add 1 c.c. or more of hydrofluoric acid which promptly gives a complete solution. 60 c.c. of 1 : 3 sulphuric acid are poured into the dish, the watch glass is removed and the solution is evaporated to heavy fumes to remove the hydrofluoric acid. The sulphates are dissolved in water and transferred to a 600 c.c. beaker and the analysis completed as in low silicon ferro-vanadium.

Ferro-vanadiums containing from 0.5 to 6.0 per cent of copper present a slight obstacle. When the ferricyanide indicator is added copper quickly produces a light yellow cloud of copper ferricyanide that entirely prevents any end point being seen. In such cases a trial analysis is run and a trial amount of the indicator is added just before filtering off the excess of manganese. The copper is thus filtered out with the manganese. The filtrate is proceeded with as usual and, if no further clouding results on adding 0.6 c.c. more of the ferricyanide indicator, the titration is completed. Should more clouding occur the analysis is repeated and twice as much indicator is added before filtering off the manganese oxide. More indicator is added to the filtrate and the analysis completed in the regular manner. Copper can be separated readily with hydrogen sulphide or by

means of potassium sulphocyanate and sulphurous acid, but more time is required and nothing gained. None of the foregoing tests need consume more than two hours except when much silicon is present and resort to hydrofluoric acid is necessary.

As ferro-vanadium samples are, at times, quite variable it is always best to make several tests of the latter and report an average of the results obtained. If the copper content does not exceed 0.3 to 0.4 per cent, even when two grams of sample are taken, the vanadium can be titrated before the clouding begins if it is proceeded with as quickly as possible after the addition of the ferricyanide.

**Small Amounts of Vanadium.** For the determination of small amounts of vanadium, ranging from 0.02 to 0.05 per cent, it is expedient to dissolve from 6 to 8 grams\* of the steel for analysis. Such large weights of steel are treated first with 60 c.c. of 1 : 3 sulphuric acid and 100 c.c. of water. When this action is over, 120 c.c. of 1.20 nitric acid are added to complete the solution and to oxidize the iron. Then continue the analysis as usual. Blanks should be carried along with equally large amounts of a plain carbon non-vanadium steel. The writer would advise against the addition of manganese sulphate to discharge any persistent pink color when boiling with permanganate as its use, in the method as given, seems to increase blanks, apparently causing part of the permanganate to pass into solution in the manganic condition. Even the blank filtrates have a brown tint as though containing a few hundredths of one per cent of chromium. This would seem, in a measure, similar to the solution of iron hydrate in iron salts. On discontinuing the use of the manganese sulphate, lower and more uniform blanks and freedom from brown tints, therein, were attained.

If pink colorations occur due to excessive additions of the permanganate, dilute further with distilled water and a drop

\* As much as 40 grams of steel can be dissolved, and the bulk of the iron removed with BaCO<sub>3</sub>, as for Al as given on page 146. Fuse the ash as directed; add the solution of the fusion to the main filtrate; convert to nitrates and finish as above for V.

or two of ferrous sulphate and boil until they are destroyed. It is rare that distilled water does not contain enough traces of organic matter to accomplish this purpose. A pink color in the analysis of ferro-vanadium does no harm in the determination of vanadium as the sulphate standard is added at the start; and the vanadium is calculated from the amount of permanganate required to produce an old rose shade, after getting the blue with the sulphate standard and ferricyanide indicator.

#### CARBON.

The high carbon, low silicon ferro-vanadiums decarbonize readily in the electric furnace with oxygen only. The lower carbon grades and high silicon varieties yield better if they are mixed with an equal weight of red lead, if burned in the electric furnace, or with four times their weight of red lead in the ten-burner Bunsen combustion furnace.

#### NICKEL.

Large amounts of vanadyl salts in solution yield ammoniacal citrates of a very dark green color, making it an impossibility to see end points in a cyanide and silver titration. The *vanadic* salts are free from this objection: Dissolve one gram of the ferro-vanadium in a mixture of 30 c.c. of 1 : 3 sulphuric acid and the same quantity of 1.20 nitric acid. Use a little hydrofluoric acid and then evaporate to fumes with sulphuric acid, as already described in this chapter, if there should be an insoluble residue after heating with the mixed acids first mentioned. Boil the sulphuric and nitric solution, or the water solution of the fumed residue, with an excess of permanganate; filter out the oxide of manganese; wash it with sulphuric acid water. Neutralize the free acid in the filtrate with ammonia *before* adding the citric acid \* or the latter will reduce the vanadic to hypovanadic acid again. Then add a slight excess of ammonia to the clear solution and titrate the nickel in the regular way

\* It is still better to add ammonium citrate made by neutralizing the citric acid with ammonia. This does away, entirely, with the vanadium green.

with cyanide and silver nitrate. (See Chapter IX.) If copper is present it will interfere and the method given in Chapter VIII, part 2, is the simplest way to prevent the interference due to copper, and, also, affords an expeditious plan to obtain the percentage of the latter element in the same analysis.

#### MANGANESE.

The manganese is obtained as in steels, by dissolving 0.050 to 0.100 gram of sample in 40 c.c. 1.20 nitric acid, boiling off red fumes, further boiling for four minutes with lead peroxide of a light brown color. Very dark brown to black looking lead peroxide should be rejected, as the black looking variety invariably gives low results. In the writer's experience with different lots, the black-brown peroxide gives results from ten to twenty per cent too low. After boiling four minutes with the brown peroxide the solution is promptly put into cool water and from there into cold water. After the excess of lead peroxide has been allowed to settle for ten minutes, or more, if convenient, the pink solution is carefully decanted into a 5 ounce beaker and titrated with a standard solution of sodium arsenite until the pink shade is gone and the slight yellow of the nitrate of iron appears.

Chromium gives high results by the process just described and must first be removed as follows: Dissolve 0.150 or 0.30 gram of the chrome or chrome-vanadium steel in 5 c.c. of 1 : 3 sulphuric acid in a 250 by 25 mm. test tube, warming gently till action is over. Warm further with 10 c.c. of 1.20 nitric acid and boil off red fumes. Cool to room temperature; dilute to about 30 c.c. with water. Add a rather thick cream of zinc oxide until the ferric and chromic hydrates begin to settle, leaving a ring of clear fluid on the top. Cool again and dilute to the 75 c.c. mark. Close the tube with a clean rubber stopper and mix the contents of the test thoroughly by repeated inversions of the tube. After the precipitate has settled somewhat, filter through a dry filter into a dry beaker. Rinse a 25 c.c. pipette 3 times with some of the filtrate and then deliver 25 c.c. into a 250 by 25 mm. test tube, add 15 c.c. of concentrated

nitric acid, bring to boil, add lead peroxide, boil four minutes and finish as in plain steels. This process can be carried through in forty-five minutes and is entirely accurate for technical analysis to two per cent of manganese. The author has encountered ferro-vanadium with as much as 5 per cent of manganese together with high silicon. In such cases a gram of the substance is fused exactly as though aluminum were being sought for. The water solution of the melt is warmed with alcohol (a few drops) until all green colorations are discharged. The insoluble residue is filtered out; washed with sodium carbonate water; dissolved off the filter with hot 1 : 1 hydrochloric acid; evaporated to thick fumes of sulphuric acid in a porcelain dish. The residue is dissolved with water, transferred to a liter flask, diluted to 500 c.c., precipitated with zinc oxide; diluted to one liter and finished as in high manganese in ferro-titanium.\* (See page 48.)

#### HIGH SILICON AND LOW MANGANESE FERRO-VANADIUM.

Such ferros cannot be analyzed for manganese as in steels on account of partial insolubility in nitric acid. Dissolve 0.100 gram of the alloy in a small porcelain dish or crucible, as far as possible, with 10 c.c. 1.20 nitric acid. When action is over add hydrofluoric acid drop by drop until, with a little further heating it dissolves all to a clear solution and no gritty or metallic particles remain. Add 20 c.c. 1 : 3 sulphuric acid and evaporate to thick fumes. Cool and dissolve the sulphates in 10 c.c., or more, if necessary, of water, heating until clear solution is attained. Wash into a 10 by 1 inch test tube. Dilute to 20 c.c. with water. Add 10 c.c. of conc. nitric acid. Boil with brown lead peroxide and finish as in steels. High silicon ferro-vanadium with manganese above 2 per cent could be assayed by taking 1.0 gram of sample. Heat with 30 c.c. 1.20 nitric acid. Clear all insoluble matter with hydrofluoric acid. Add 60 c.c. 1 : 3

\* Or finish by the author's method given on page 278 for manganese above 2 per cent.

sulphuric acid. Evaporate to thick fumes. Dissolve in water. Transfer to a liter flask. Dilute to about 500 c.c. with water. Add a slight excess of zinc oxide. Dilute to the liter mark. Mix thoroughly and finish as given for high manganese in ferrotitanium. (Page 48.)

#### SULPHUR.

Ferro-vanadium does not dissolve completely in dilute hydrochloric acid so that even approximate sulphur tests by evolution are not available. To determine sulphur in low silicon ferro-vanadium dissolve three grams of sample in one hundred c.c. of concentrated nitric acid in a 600 c.c. beaker. When action ceases add immediately 50 c.c. of concentrated hydrochloric acid for, in alloys containing thirty-five and higher percentages of vanadium, a red precipitate settles out in large quantities if hydrochloric acid is not present to dissolve it. The presence of the red precipitate has a disadvantage. It causes the contents of the different beakers to spurt. Two grams of carbonate of soda are added. The solutions are transferred to No. 6 porcelain dishes and evaporated to dryness. The residue is dissolved in 100 c.c. of hydrochloric acid and evaporated again to dryness. Solution is once more effected with 50 c.c. of conc. hydrochloric acid followed by evaporation to a scum. Ten c.c. of concentrated hydrochloric acid are employed to dissolve the scum; 100 c.c. of water are added; the solution is filtered; diluted to 300 c.c. and the sulphate precipitated with barium chloride, using 60 c.c. of a saturated solution diluted with 240 c.c. of water. Blank determinations are made of exactly the same reagents and the sulphur found is deducted.\*

One gram of highly silicious ferro-vanadium is fused with a mixture of 20 grams of sodium carbonate and four grams of potassium nitrate. The fusion is dissolved in water, acidulated with hydrochloric acid, evaporated twice to dryness,

\* Or fuse 1 gram with 8 grams of  $\text{Na}_2\text{O}_2$  in an iron crucible; dissolve in water; acidulate with HCl, etc.

taken up with 20 c.c. of concentrated hydrochloric acid and sufficient water to dissolve the sodium chloride, and filtered. The sulphate in the filtrate is precipitated with barium chloride solution.

#### ALUMINUM.

Aluminum cannot be separated from vanadic solutions by ammonia. The latter are not precipitated by ammonia alone, but if iron or aluminum be precipitated in the presence of vanadic or vanadyl salts, large quantities of the element are carried out of solution by the iron or aluminum in a manner analogous to the precipitation of phosphoric acid by means of ferric salts and ammonia.

The following procedure gives a highly satisfactory separation. Fuse 0.815 gram of ferro-vanadium in a mixture of 10 grams of sodium carbonate and two grams of potassium nitrate. Raise the heat very gradually. Keep molten for a half hour. Dissolve the melt in water; mix with filter-paper pulp; filter; wash with water containing a little sodium carbonate. Return the washed residue to the crucible in which the fusion was made; roast; and fuse it again with the same mixture.\* Dissolve the fusion in hot water, preferably in a platinum dish; cool; add paper pulp made from ashless filter paper; filter and wash as before. Combine the two filtrates, heat same almost to boiling, volume being about 600 c.c.; remove from flame; add from a burette 1 : 1 hydrochloric acid, i.e., 1.093 specific gravity at 29° C. Hold the cover on the beaker in an inclined position to permit of stirring without loss of spray. Continue the addition of the acid until aluminum hydroxide begins to cloud the solution. This will occur when about 45 c.c. of acid have been dropped in. Now add the acid  $\frac{1}{2}$  c.c. at a time, stirring thoroughly, until turmeric paper is no longer turned, quickly, to even a faint brown by the solu-

\* When large amounts of Al and Fe are present, a third or even a fourth fusion is necessary. In such instances the second method is preferable. (Page 23.)

tion. The solution will still be somewhat alkaline, but it is essential to a good separation that it be so. Very small amounts of aluminum hydroxide settle slowly, requiring several hours to collect, and giving, at first, only a faint cloudiness in the solution. Mix with the precipitate a quantity of paper pulp about equal to the volume the precipitate would occupy if it were drained on a filter. A wad about 1 inch in diameter is sufficient in most cases. Wash with ammonium nitrate water (1 gram of the salt dissolved in 100 c.c. of water). If the mixture of pulp and aluminum hydroxide, after being washed 15 or 20 times, is not entirely free of yellow tint, it should be dried; the paper burned off in the platinum crucible and the residue fused once more with  $\text{Na}_2\text{CO}_3$ , only, and treated exactly as before, i.e., dissolved in water and precipitated with 1 : 1 hydrochloric acid. This insures a snow white precipitate, free of vanadium. The aluminum hydroxide being now free of vanadium is dissolved off the filter with 50 c.c. of hot 1 : 1 hydrochloric acid. The hot acid is poured on the pulp six times, reheating the solvent at each pouring. The paper pulp is washed free from chlorides with water. The filtrate and washings are heated to boiling, and the aluminum hydroxide is precipitated in the usual way with a slight excess of ammonia, paper pulp added and the hydroxide washed, roasted and blasted to a constant weight as  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{SiO}_2$ .

Test all of the filtrates mentioned in the foregoing outline by adding an excess of acid and then a slight excess of ammonia to make certain that the various manipulations have been properly conducted.

The writer has repeatedly observed in making the separation of much aluminum from much, or indeed any, vanadium that if the neutralization of the hot sodium carbonate fusion be carried farther than here given the aluminum hydroxide will contain vanadium. In short, make sure that the solution is still distinctly alkaline. To guard against presence of silica it is well to add 10 c.c. of hydrofluoric acid and a few drops of

sulphuric acid to the  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{SiO}_2$ . Evaporate; ignite; and weigh again.\*

The phosphorus in the precipitate is estimated and deducted as follows: Fuse the precipitate with 10 grams of sodium carbonate; dissolve in water; precipitate with 1 : 1 HCl as described; dissolve off the filter with 50 c.c. of hot 1 : 1 hydrochloric acid and wash free of chlorides as usual. Evaporate to 5 c.c.; add 100 c.c. of concentrated nitric acid; evaporate again to 10 c.c. Dilute with 20 c.c. of water; filter through a small filter and wash with very dilute nitric acid. Evaporate the filtrate and washings to 50 c.c.; boil with a slight excess of permanganate of potash; clear with a small excess of ferrous sulphate followed by an addition to the still hot solution of 50 c.c. of molybdate solution. Finish as in phosphorus in steels; calculate to  $\text{P}_2\text{O}_5$  and deduct from the weight of silica free  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ . The remainder is the pure  $\text{Al}_2\text{O}_3$ . The acid precipitation of aluminum hydroxide is an application of the well-known reaction,  $\text{Al}(\text{ONa})_3 + 3 \text{HCl} = 3 \text{NaCl} + \text{Al}(\text{OH})_3$ . Treadwell mentions that W. F. Hillebrand recommends this separation of aluminum from small amounts of vanadium found in ores of iron and in rocks. The writer has never had the pleasure of reading Hillebrand's article. The reference is given as *American Journal of Science* (4), VI, p. 209.

#### PHOSPHORUS.

Vanadium precipitates with the phosphorus if an attempt be made to determine the percentage of the latter element by a molybdate separation as ordinarily practiced in steel analysis. The phospho-molybdate is colored by presence of vanadium, being of a rather dark orange color. Further, in the presence of much vanadium most of the phosphoric acid is *not* precipitated by the molybdate solution as used in steels.

\* Blanks must be made including all fusions, acidulations, evaporation and every other step in the foregoing scheme as the chemicals are almost certain to be impure; and glassware and dishes are more or less attacked.

Having noted vagaries that have been commented on by several authors of works on the analysis of iron and steel, and not having read any suggestion that improved the situation, some experiments were made to study the matter. First the boiling of the nitric acid solution of the alloy with a very slight excess of potassium permanganate and then clearing with just one drop of ferrous sulphate was tried, that is, a precipitation in the presence of *vanadic* acid. Second, as before, except that a large excess of ferrous sulphate was added after boiling with permanganate, being a precipitation in the presence of *vanadyl* salt. These two conditions were further modified by varying the length of time between the addition of the molybdate solution and the subsequent filtering out of the yellow or, rather, red precipitate. The discordant results are given in Table I, together with the actual phosphorus as obtained by the writer's aluminate method (page 22).

From such results, and others not given, it was decided to remove the vanadium entirely from the phosphorus and then precipitate with molybdate. As iron carries large quantities of vanadium with it when precipitated in the presence of the former element by ammonia, phosphorus could not be separated as ferric phosphate. A number of other schemes were resorted to, and finally the following plan proved successful, and demonstrated, as given in the table, that as little as one-fourth of the phosphorus is, at times, obtained by the ordinary methods as given in the most recent books on the analysis of steel works materials.

A solution of sodium aluminate was prepared by placing 10 grams of metallic aluminum in a large dish (platinum preferred) together with 50 grams of stick caustic soda. Water was added a drop at a time as the action proved extremely violent, much heat being generated. When the reaction was complete the mass of aluminate was dissolved in water; some paper pulp was added; the solution was filtered, and the filtrate and washings were diluted to 520 c.c.

A double fusion using 10 grams of sodium carbonate and 2 grams of potassium nitrate, each time, is made of 0.815 gram

## CHEMICAL ANALYSIS OF SPECIAL STEELS

TABLE I.

Grade of Pero-V. Per cent V.	Weight Taken. Grams.	Amount of Excess of Ferrous Sul- phate.	Time Elapsing Between the Addition of the Molybdate and the Filtering out of the Phospho-Molybdate Precipitate.	Phosphorus Found by the Several Variations of the Ordinary Method; and Color of Precipitate.	The Phosphorus as Found by the Author's Aluminate Method; Color of Precipitate.
No. 124. 11% V.	0.815	None	1 hour	0.322% red	{ 0.427% phosphorus 0.404% Bright yellow
No. 124 No. 124	0.815 0.815	None Large	24 hours 24 hours	0.214% Very red	{ 0.242% 0.258% 0.247% Bright yellow
No. 4. 52.50% V. No. 4 No. 4 No. 4	0.815 0.500 0.815 0.815 0.500	None None Large Large Large	1 hour 1 hour 24 hours 24 hours 1 hour	0.060% red 0.062% red { 0.120% 0.166% Very red 0.130% red	{ 0.242% 0.258% 0.247% Bright yellow
No. 134. 57.5% V.	0.815	None	1 hour	0.036% red	0.233%
No. 134 No. 134 No. 134	0.815 0.815 0.815	Large None Large	1 hour 25 hours 25 hours	0.022% red 0.152% 0.122 Very red	0.234% 0.236% 0.235% Bright yellow

of the powdered sample in exactly the same manner as just described for the aluminum separation. Add to the combined filtrates and washings from the iron residue 5 c.c. of the sodium aluminate solution and precipitate it with 1 : 1 hydrochloric acid, adding the acid until the solution no longer changes turmeric paper, at once, to even a faint brown.

The precipitated aluminum hydroxide and phosphate are washed 15 times with ammonium nitrate solution, roasted in a platinum crucible, and fused again with 10 grams of  $\text{Na}_2\text{CO}_3$  + 2 grams  $\text{KNO}_3$ . The melt is dissolved in water, and precipitated again with 1 : 1 hydrochloric acid as described under aluminum. This precipitate is then washed, converted into nitrate, and the phosphorus is separated with molybdate solution. It is a bright yellow, totally free of red tint. The extent to which vanadium holds phosphorus in solution is shown by the results obtained, which are also given in the table for convenient comparison. The United States Bureau of Standards pig iron "B" was dissolved in 1.20 nitric acid, evaporated, ignited to a dull red, dissolved in hydrochloric acid, precipitated with ammonia; washed; roasted in a platinum crucible and treated as though it were a ferro-vanadium. The phosphorus was obtained by the aluminate and acid scheme. A laboratory standard was tested in like manner for phosphorus. The correct phosphorus was obtained in each sample.

#### SECOND METHOD FOR ALUMINUM AND PHOSPHORUS IN FERRO-VANADIUM.

Dissolve one gram of sample in 40 c.c. 1.20 nitric acid. If there remains an insoluble metallic residue when the percentage of silicon is high, filter out the undissolved part. Wash it with 1.20 nitric acid. Roast off the paper pulp. Fuse it with twenty times its weight of  $\text{Na}_2\text{CO}_3$  plus one-fifth its weight of potassium nitrate. Dissolve the melt with water in a platinum dish. Transfer the water solution to a porcelain dish; add an excess of 1 : 1 hydrochloric acid. Heat until all is dissolved. Clean the crucible with 1 : 1 hydrochloric acid when all is in solu-

tion. Transfer the acidulated fusion and the cleanings of the crucible to a 1000 c.c. boiling flask. Also add to the same, the filtrate and washings from the residue that remained undissolved in nitric acid. Dilute to about 300 c.c. Hold the flask in one hand, and project into it with the other hand, from a small porcelain spoon, sodium peroxide, a gram or two at a time. When sufficient peroxide has been added to precipitate all of the iron, then add an excess of 10 grams of the former; also 10 grams of sodium carbonate to supply carbon dioxide. Boil twenty minutes; cool and filter out the iron hydroxide, mixing with it a large amount of paper pulp. Wash this mixture on the filter with sodium carbonate water twenty times. The filter should be a double 12 cm. one. The strongly alkaline solution is diluted with 100 c.c. of water before the iron hydroxide is filtered from it. Each washing is well drained off before the next one is added. A small square of cheese-cloth is folded in with the filter at the apex to prevent the alkaline solution from tearing the paper. This filtrate and washings are designated A.

Dissolve the iron residue off the filter and treat it with peroxide and 10 grams of carbonate exactly as before, obtaining filtrate B.

#### PHOSPHORUS.

(A) Heat the filtrate and washings from the iron hydroxide obtained in the first peroxidation; add 5 c.c. of the aluminate solution. Mix well. Then introduce 1 : 1 hydrochloric acid as described in the first method for phosphorus. Keep the solution slightly but distinctly alkaline. The acid is added until the solution no longer gives turmeric paper a *faint* brown tint, *quickly*. Filter off the aluminum hydroxide, mixing paper pulp with it. Dissolve the hydroxide off the filter with 40 c.c. of 1 : 1 hydrochloric acid, after first washing 15 times with ammonium nitrate water. Pour the hot acid back and forth over the pulp six times, heating the acid before each pouring. Wash the pulp free from chloride test with water.

The filtrate and washings from the pulp are peroxidized, also. This time add only enough peroxide to insure alkalinity and to dissolve any aluminum hydroxide that may appear. Boil the solution 10 seconds, adding 10 grams of sodium carbonate before boiling. Remove from the flame and precipitate as before with 1 : 1 HCl. Filter off aluminum hydroxide and finish as given for phosphorus in the first method. Add a slight excess of acid to the filtrate and washings; then a faint excess of ammonia to make sure that all aluminum hydroxide has been precipitated. The aluminum hydroxide is put through this second peroxidation to remove any vanadium that is carried down with it the first time it is precipitated with acid. It should now look pure white, free from any suggestion of yellow tint. If it has a yellow color, too much acid has been used in its precipitation. In that event it must be dissolved off the filter and peroxidized again, but unless proper degree of alkalinity is observed it will still appear yellow.

(B) The filtrate and washings from the second peroxidation of the iron are treated with 5 c.c. of aluminate solution and then as described for those obtained from the first peroxidation; but as practically no vanadium is present in the second peroxidation, this aluminum hydroxide is free of any vanadium and can be dissolved off the filter and converted into nitrate at once to obtain the remainder of the phosphorus.

(C) The iron residue after its second peroxidation is dissolved off its filter with hot 1.20 nitric acid, pouring the acid back on the filter six times, stirring up the pulp each time with a glass rod. Wash 40 times. Evaporate filtrate and washings to 40 c.c. Boil with permanganate and finish as in steels. Only a few thousandths of a per cent of phosphorus are found with the iron, even with a phosphorus content of 0.24 per cent.

This method avoids all fusions except one, and that one is necessary only in high silicon ferros. It checks perfectly with the first method and is really an outgrowth of it. However, it requires more of the operator's time in that he cannot give his attention to much else while making the peroxidations.

It is an economy of platinum rather than of time.\* If, after removing the vanadium by either the first or second methods for phosphorus, the phospho-molybdate still retains an orange shade rather than a light canary yellow, vanadium is still present to some extent, and a considerable portion of the phosphorus is surely held in solution. It means that some part of the directions have not been exactly followed. The trouble is almost certain to be due to having precipitated the aluminum hydroxide in too faintly alkaline solution. For example, if the color of the phospho-molybdate suggests even a slight red and the precipitates tend to adhere to the bottom of the beaker, a result of 0.19 per cent may be obtained when the actual phosphorus is 0.25 per cent.

As the amount of phosphorus remaining with iron after the first peroxidation is very trifling for all practical purposes, it is not necessary for steel works, or indeed most technical analysis, to make a second peroxidation of it. In this way it is simply necessary to make the one peroxidation to remove iron, and the total phosphorus is then separated from the vanadium in the filtrate as given. However, should more than 0.25 per cent phosphorus be found, it would be safer to follow the entire method as first described.

Add 0.100 gm. of aluminum dissolved in hydrochloric acid or 5 c.c. of aluminate solution for every 0.25 per cent of phosphorus supposed to be present in the ferro.

#### ALUMINUM.

Proceed exactly as for phosphorus, but add no aluminate. Any precipitate that forms with 1 : 1 HCl is then treated as described in the first method for aluminum. This process avoids all fusions except the one required when silicon is high. A blank must be run, imitating the test in every detail. A plain carbon steel can be used for the blank, weighing out approximately as much of it as there is supposed to be iron present in

\* It can be used to advantage when a number of samples are assayed at the same time.

the ferro. This separation of aluminum from vanadium and iron has been tested by the author with mixtures containing as much as 10 per cent of aluminum and 50 per cent of vanadium, the remainder being iron, on a one-gram basis.

A good way to run a blank for either aluminum or phosphorus is to dissolve 100 mgs. of metallic aluminum of known aluminum content in a few c.c. of hydrochloric acid. Add this to 400 mgs. of a plain carbon steel. Put the mixture through the entire analysis. Deduct the excess of aluminum found from the aluminum obtained from the ferro. The remainder will be the aluminum sought in the ferro-vanadium.\* Deduct the phosphorus found in this blank test from that found by the same process in the ferro, allowing for the phosphorus known to be in 0.400 gram of steel used.

Instead of using the aluminate solution for the phosphorus determination, 100 mgs. of aluminum can be added, after dissolving it in a few c.c. of 1 : 1 hydrochloric acid, whenever the foregoing directions call for 5 c.c. of aluminate. In this way the aluminum and phosphorus can be gotten from the same analysis. It is merely a matter of deducting from the total aluminum found, the aluminum added, and also the blank. Add 100 mgs. of aluminum dissolved in hydrochloric acid for every 0.25 per cent of phosphorus when one gram of sample is taken for analysis. The phosphorus is gotten last by fusing the  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$  after it has been weighed in the silica free condition. Fuse the oxides with sodium carbonate, using 10 grams. Dissolve the melt in water. Precipitate the water solution as usual with 1 : 1 hydrochloric acid. Filter off the aluminum hydroxide, etc. Wash it a few times. Mix paper pulp with the hydroxide to hasten filtration and washings. Dissolve the hydroxide off the filter with 50 c.c. 1 : 1 hot hydrochloric acid as previously described in the first method. Wash the pulp free of chlorides. Evaporate the filtrate and washings to about 10 c.c.

\* For example if 0.100 gm. of 99.5 per cent aluminum is added to 400 mgs. of a plain steel and 0.110 gm. is recovered by the method, then the blank would be 0.110 - 0.0995 or 0.0105 gm.

Add 100 c.c. of conc. nitric acid and evaporate to 15 c.c. Rinse into a 5 oz. beaker. Boil with permanganate solution and finish as in steels.

As considerable silicic acid is obtained from the operations in this second method, it is better to remove the silicon by evaporating the aluminum chloride, etc., to dryness just before precipitating it to weigh it as  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ . This avoids the use of hydrofluoric acid.

A single peroxidation is not sufficient to separate the aluminum from the iron. A little is always found in the filtrate from the iron hydroxide after its second peroxidation.\*

#### IRON.

The iron residue obtained from fusions for aluminum or phosphorus is roasted free of paper; dissolved with hydrochloric acid. The crucible in which the fusions were made is cleaned by warming a little of the same acid in it. The cleanings are added to the main solution of the residue. Sixty c.c. of 1 : 3 sulphuric acid are introduced, and the solution is evaporated to thick fumes. The residue is dissolved in 300 c.c. of water, and hydrogen sulphide is passed through it until the various sulphides have settled out well. The reduced iron is filtered free of sulphides into a round flask. Hydrogen sulphide is again passed through the solution to reduce any iron that may have become oxidized during filtering and washing. The hydrogen sulphide is removed by boiling the solution with carbon dioxide passing rapidly through it. When the gases coming from the hot flask no longer cause filter paper moistened with lead acetate to turn brown or black, the flask is cooled in water with carbon dioxide still passing. When cold the solution is titrated with a potassium permanganate standard, 1 c.c. of which equals 0.00556 gram of iron, made by dissolving 3.16 grams of c.p. permanganate in water and diluting to one liter. (See Standardization of  $\text{KMnO}_4$ , page 49.)

\* If the Al present is found to exceed 10 per cent, it is safer to make a third peroxidation.

The writer frequently uses the plan of dissolving the ferro in sulphuric and nitric acids, with a little hydrofluoric acid if necessary. Evaporation to fumes and solution in water are the next steps. The vanadium and iron are then reduced with hydrogen sulphide, the solution is filtered,\* hydrogen sulphide is removed with  $\text{CO}_2$ , and permanganate of potash standard is added until a pink is obtained or an old rose shade, that does not fade perceptibly after one minute's stirring. 2.5 c.c. of ferricyanide indicator are now dropped in, and a ferrous ammonium sulphate standard, 1 c.c. of which equals 1 c.c. of the permanganate, is added until three drops of this standard cause the light blue of the vanadyl solution to darken with the blue of the ferricyanide of iron. The number of c.c. of permanganate used to produce the old rose shade less the number of c.c. of sulphate required equals the number of c.c. of permanganate used to oxidize the iron, which number multiplied by 0.00556 gives the amount of iron in parts of a gram. The number of c.c. of sulphate used to produce a darkened blue, multiplied by 0.00508 (provided the sulphate exactly equals the permanganate), equals the number of grams or parts of a gram of vanadium present.

The iron residue from the carbonate and niter fusions may be proceeded with for the estimation of the latter metal in this way: After removing the platinum, copper, etc., from the hydrochloric acid solution of the iron oxide by hydrogen sulphide, evaporate the filtrate and washings from the sulphides with a small excess of potassium chlorate. Remove the hydrochloric acid by evaporation to thick fumes with 60 c.c. 1 : 1 sulphuric acid. Add water; dissolve by heating; reduce with metallic zinc; and titrate with standard permanganate for iron.

#### COPPER.

If copper is present to any appreciable extent, as shown by the clouding with the ferricyanide indicator, it can readily be

\* Immediately after filtering out the sulphides, pass  $\text{H}_2\text{S}$ , again, for 30 minutes to reduce any iron that may have become oxidized during the filtration and washing of any metallic sulphides that may have formed. Then pass  $\text{CO}_2$  to remove the excess of  $\text{H}_2\text{S}$  as above.

separated by hydrogen sulphide, passing the latter gas through the sulphate solution obtained by dissolving the sample in nitro-sulphuric acid, using a little hydrofluoric acid if much silicon be present, evaporating to fumes of sulphuric acid and dissolving in boiling water to hasten solution. Copper can also be easily and quickly separated from this sulphate solution by neutralizing most of the free acid and precipitating the copper with an excess of potassium thiocyanate and sulphurous acid. (Also see the author's ferricyanide separation.) The sulphide of copper is filtered, washed with hydrogen sulphide water, roasted free of paper in a porcelain crucible, dissolved in 1.20 nitric acid, and filtered from any insoluble sulphides or alumina. The filtrate and washings are made slightly alkaline with sodium carbonate water; one c.c. of ammonia is added and the solution titrated to disappearance of a blue with potassium cyanide standardized against 99.8 per cent metallic copper in the same manner.

Chromium, as already intimated, when present, can be determined in the presence of vanadium and in the same operation.

In steels the amount of double sulphate used to discharge all red colorations, leaving the solution a clear light green, free of all yellowish tints, less the number of c.c. of the permanganate standard required to produce a slight permanent pink reflection, thereafter, equals the amount of double sulphate necessary to reduce the chromic acid present to chromic sulphate. One c.c. of the double sulphate usually equals 0.00087 gram of chromium. As already explained, the ferricyanide indicator is now dropped in, and the sulphate standard again follows until three drops of it produce a blue.\* The amount of sulphate consumed by this last titration is equivalent to the vanadic acid present, after deducting the regular blank, which is usually 0.4 to 1.0 c.c., depending on the amount of chromium. A sample calculation is given as an illustration. (2 grams are taken for analysis.)

\* The sulphate standard is now added until three drops of it change the dark green to a blue.

## ANALYSIS OF VANADIUM STEEL AND FERRO-VANADIUM 31

### FIRST PART OF THE TITRATION TO OBTAIN THE CHROMIUM. (MADE BEFORE ADDING FERRICYANIDE.)

KMnO <sub>4</sub>		Double Sulphate.
9.1 c.c.	second reading of burette	28.6 c.c.
2.3 c.c.	first reading of burette	12.4 c.c.
6.8 c.c.		16.2 c.c.

### CALCULATION.

16.2  
6.8

9.4 c.c. equal sulphate used by chromium.  
 $9.4 \times 0.00087 \times 100 \div 2 = 0.4089$ , or per cent chromium.

### SECOND PART OF THE TITRATION (MADE IMMEDIATELY AFTER ADDING THE FERRICYANIDE INDICATOR) TO OBTAIN THE VANADIUM.

#### *Sulphate.*

31.4 c.c. second reading of burette.  
28.6 c.c. first reading of burette.  
2.8 c.c.  
0.4 c.c. equals regular vanadium blank for low per cent chromium.  
2.4 c.c.

Since 1 c.c. of sulphate equals 1 c.c. of permanganate or 0.00254 gram of vanadium, therefore  $2.4 \times 0.00254 \times 100 \div 2 = 0.305$  per cent vanadium.

### SMALL AMOUNTS OF CHROMIUM.

Ferro-vanadium frequently, as stated, contains one or two tenths of a per cent of chromium. The most satisfactory way to estimate these small amounts, in the presence of large per cents of vanadium, is to fuse 1 gram of the finely ground powder or thin drillings with 20 grams of sodium carbonate and 4 grams of niter. After the fusion is quiet, keep it molten for thirty minutes. Dissolve the melt in as little water as possible in a platinum or porcelain dish. Add pulp; filter; wash with sodium carbonate water. Evaporate the filtrate and washings to about 40 c.c. If the solution is not clear, add a little pulp, filter and wash again. The filtrate and washings should not exceed 40 to 50 c.c. if the chromium content is only a tenth of a per cent or thereabout. Compare this solution with a standard consisting of 0.070 gram of c.p. potassium dichromate made slightly alkaline

with sodium carbonate and diluted to 250 c.c. in a volumetric flask. It is made alkaline by adding sodium carbonate until the red color of the dichromate has all been converted into the yellow of the sodium chromate. 1 c.c. equals 0.0001 gram of chromium. Use the same comparison tubes as described under the color method for titanium. Rinse one of the tubes three times with some of the standard. Then pour into it exactly 10 c.c. of the standard solution. If the chromium content is about 0.20 per cent, the standard will be yellower than the test. Add water to the standard, 1 to 2 c.c. at a time, until its color is only slightly stronger than that of the test. Continue the addition of water in  $\frac{1}{2}$  c.c. amounts until the standard is just turned lighter than the test. Suppose the standard matches the test in color at 27.5 c.c. and the volume of the test is 59.5 c.c. This gives the proportion:

$$\begin{array}{lll} \text{Standard Vol.} & \text{Test Vol.} & 10 \text{ c.c. Std.} \\ 27.5 & : & 59.5 : : 0.001 : X \\ 5.95 \div 27.5 = 0.21, \text{ or } 0.21 \text{ per cent chromium.} & & \end{array}$$

#### MOLYBDENUM.

\* Molybdenum is separated exactly as the copper with hydrogen sulphide in slightly acid solution. The brown sulphide is roasted at a low heat in a porcelain crucible to a white or a bluish white residue (unless dark colored oxides are present, such as copper). The white oxide is brushed into a platinum crucible, fused with ten times its weight of sodium carbonate; dissolved in water; two drops of methyl orange are added, and then hydrochloric acid until one drop produces a pink. Add 1 c.c. of conc. hydrochloric acid in excess. Heat the solution to boiling. Precipitate the molybdenum in the hot solution with lead acetate. Add also an equal volume of a solution of ammonium acetate (50 grams of the salt made to a volume of 100 c.c. with water). Let the precipitate settle for an hour or two. Cool. Filter. Wash with hot water. Ignite in a plat-

\* The molybdenum can be weighed, also, as the trioxide as given under molybdenum steels.

inum crucible at a low red heat. Cool and weigh as lead molybdate, which multiplied by 26.16 and divided by the weight taken for analysis gives the per cent of molybdenum. (See Molybdenum in Steel, page 130.)

#### SILICON.

For silicon dissolve one gram of the finely ground ferro in 50 c.c. 1:20 nitric acid. Add 30 c.c. 1:3 sulphuric acid and evaporate to fumes. Dissolve the sulphates in water, heating until all but silicic acid is in solution. Filter. Wash with dilute hydrochloric, then with water. Ignite and weigh as usual. If the sample contains much silicon and does not yield to the nitric acid, filter out the insoluble residue; wash it first with hydrochloric acid and then with water; roast off the paper in a platinum crucible. Fuse the residue with 20 times its weight of sodium carbonate plus  $\frac{1}{6}$ th its weight of potassium nitrate. Dissolve the melt with water. Acidulate it with hydrochloric acid and add the clear solution to the portion dissolved by the nitric acid, and evaporate all to fumes with 30 c.c. of 1:3 sulphuric acid, and finish as in low silicon ferro-vanadium.

#### STANDARDIZATIONS.

The writer prefers to standardize permanganate of potassium against recrystallized oxalic acid kept in tightly stoppered bottles: \* 1.58 grams of potassium permanganate are dissolved in a liter flask with distilled water and diluted to the mark. 19.5815 grams of double sulphate of iron and ammonia, i.e.,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 + 6 \text{H}_2\text{O}$ , are dissolved in the same manner, with the addition of 50 c.c. of 1:3 sulphuric acid, and diluted to one liter. Usually the relationship between these two standards is that from 40.2 to 40.5 c.c. of the permanganate equal 40 c.c. of the double sulphate. The vanadium value of the permanganate standard is checked against the oxalic acid, and the vanadium value of the sulphate standard is calculated from its relation to the permanganate standard.

\* Keep oxalic acid in a cool place to prevent loss of water of crystallization.

\* The 1.58 grams of permanganate solution, theoretically, should be equivalent to 2.56 grams of vanadium. Its actual value is found as follows: 0.1424 gram of oxalic acid is dissolved in about 100 c.c. of water plus 20 c.c. of 1 : 3 sulphuric acid and heated to 80° C. The permanganate standard is then added until one drop produces a permanent pink. This usually requires 45.45 c.c. of the permanganate. We in the first place have the proportion:

Oxalic Acid.      Permanganate.

$$63 : 31.6 :: 0.1424 : X.$$

This gives  $X$  equals 0.07142, or 0.07142 gram of pure permanganate will oxidize 0.1424 gram of oxalic acid. By the above titration it is found that it requires 45.45 c.c. of the permanganate standard to oxidize 0.1424 gram of oxalic acid. Therefore each c.c. of the permanganate standard must contain 0.07142 divided by 45.45, or 0.001571 gram of 100 per cent potassium permanganate. We thus obtain the final proportion, or

$$1.58 : 2.56 :: 0.001571 : X.$$

$X$  equals 0.002545, or 1 c.c. permanganate solution equals 0.002545 gram of vanadium.

The chromium value of these standards is found by adding to 2 grams of a plain carbon steel a weighed amount of recrystallized potassium dichromate. This mixture is put through the entire process of an analysis. Taking the percentage of chromium in dichromate of potash as 35.38 per cent, the sulphate standard is found to have a value that varies from 0.00085 to 0.00087 gram of chromium per c.c.

It must be constantly borne in mind that to attain success in vanadium and chromium titrations, in steels, that it is absolutely essential when coming back with permanganate to stop with the first 3 drops that give a faint pink reflection that is still faintly, but distinctly, visible after *thirty seconds* stirring. Furthermore, the next step is to add the ferricyanide indicator. Then the ferrous ammonium sulphate is quickly added until 3 drops produce the first distinct darkening of the green to a

\* Read pages 41 to 42.

distinct blue. Do not continue to add the sulphate to a still darker blue. In short, if the pink end-point is overdone, and then the blue one also, the error is doubled. Always aim to finish standards, blanks and tests exactly as described.

The author has had occasion to analyze the following varieties of ferro-vanadium which will give some idea of the different types likely to be encountered by the iron and steel analyst:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6
	Per cent.					
Vanadium.....	22.77	12.45	35.15	52.5	31.48	23.33
Carbon.....	1.74	0.16	0.35	3.09	0.08	4.55
Manganese.....	0.07	0.46	0.10	0.07	0.28	3.30
Phosphorus.....	0.40	.....	.....	0.28	.....	.....
Silicon.....	0.60	7.65	1.02	0.43	13.00	3.8
Iron.....	74.08	65.54	62.60	41.50	.....	.....
Sulphur.....	.....	0.15	.....	0.52	.....	.....
Chromium.....	.....	.....	.....	0.22	.....	.....
Aluminum.....	.....	7.31	.....	.....	4.13	.....
Copper.....	.....	6.24	.....	.....	.....	.....
Molybdenum.....	.....	.....	.....	0.50	.....	.....

#### THE AUTHOR'S PRESENT METHOD OF TITRATING VANADIUM IN FERRO-VANADIUM AND PLAIN VANADIUM STEEL.

During four or more years subsequent practice of the vanadium method, given in the preceding pages of Chapter II, some changes have been made to avoid the interference of any small amounts of manganese present in the solution, in the manganic state; or chromium that may be in the sample to the extent of 0.20 to 0.10 per cent, or less; or of uranium. The latter element, when in the solution to the amount of several per cent, forms objectionable brown tints, seriously obscuring the end point if the ferricyanide indicator is added first; then the sulphate standard; and then the permanganate standard to obtain the old rose shade. Before this end point is attained, the uranium brown color has overshadowed it. By the following modification these interferences are avoided.

First from a 100 c.c. burette deliver into an 800 c.c. beaker 40 c.c. of the sulphate standard. Also pour in the beaker 350 c.c. of distilled water and 30 c.c. of 1 : 3 sulphuric acid. Titrate this mixture with the permanganate standard to get the relation between the two standards; assuming the vanadium value of the permanganate as correct, that of the sulphate is calculated from the result of this titration. The standards prepared as given on pages 33 and 34 should be nearly equivalent in vanadium value.

Now, instead of adding the ferricyanide indicator at the start, the titration is begun by adding the sulphate standard until all brown or pink tints are gone and a green color begins to appear due to the partial reduction of the vanadic acid to the hypo-vanadic state. Next, add the permanganate standard with continued stirring until a strong reddish pink is reached; stir well and wait 30 seconds to insure a complete reaction between the vanadium and the permanganate as the former acts rather slowly at room temperature; make sure that the red color does not fade perceptibly during the pause. In case a fading is noted more permanganate must be added, followed by more stirring, and so on, until the fading is no longer noticeable. However, such fading does not occur as a rule more than once, if the red end point is approached rather slowly and with much stirring after each addition of the permanganate standard.

The sulphate standard is, again, dropped in to remove the excess of the permanganate; this is accomplished by adding the former standard, a few drops at a time, until the deep red is all gone and the solution has taken on, in the main, a yellow tint with a very slight but distinct tan shade in it. At this stage 2 drops of the permanganate should cause a reappearance of a slight suggestion of pink, as one looks down through the mouth of the beaker. The operator can then discharge this very faint pink with 2 drops of the sulphate standard. The solution is now ready for the titration proper. The reading of the sulphate burette is noted; the ferricyanide indicator

is poured in, and the sulphate standard is dropped in immediately, thereafter, until the green color that forms is changed to the *first* deep blue. This dark blue is the end point, and should be rather rapidly approached to catch the first change from the dark green to the blue. Of course the solution is stirred vigorously during the titration. The sulphate used for this last titration, i.e., subsequent to the pouring in of the indicator, minus the blank, is the sulphate equivalent of the vanadium.

#### PLAIN VANADIUM STEEL.

With a vanadium content of 0.10 to 0.30 per cent, take from 4 or 5 grams of sample and proceed as described for chrome vanadium steel on page 7, using 50 c.c. of 1 : 3 sulphuric acid to effect the solution of the drillings, diluting with about 20 c.c. of water to prevent the formation of crusts of sulphate of iron; warm until no further evolution of fine bubbles of hydrogen is visible; and then add 75 c.c. of 1.20 nitric acid to oxidize the ferrous iron; heat until all red fumes are gone; proceed further as given on page 8, except that the excess of the hydrated oxide of manganese is filtered out by means of a porous alum-dum thimble, avoiding entirely the use of asbestos filters. This same filter is now used for this purpose in the analysis of ferro-vanadium. But very slight suction is required. (See photo 15, page 247.)

The filtrate and washings can be pink with an excess of permanganate as will be seen. The volume of all tests and blanks should be the same and should not exceed 350 c.c. just before the titration. Titrate the above filtrate in the same manner as given for the ferro-vanadium, i.e. discharge all pink or brown tints to a clear greenish yellow (of course the green is not so noticeable in steels as it is in ferro-vanadium) by adding, at the start, about 10 or more c.c. of the sulphate standard; then continue as in the ferro and calculate the vanadium from the sulphate required to produce the dark blue after the addition of the indicator, less the blank which for this procedure is, in this laboratory, from 0.8 to 0.9 c.c. for plain vanadium steels.

**BLANK TESTS.**

To obtain the blank test to apply in the analysis of ferro-vanadium of from 30 to 40 per cent vanadium, dissolve 200 mgs. of plain carbon steel; and for plain vanadium steels, dissolve five grams of plain steel just as directed for ferro-vanadium and plain vanadium steel, respectively. Put these blanks through all of the operations and titrations, noting the amount of sulphate required to produce a dark blue after the ferricyanide indicator has been added in the order given. The portion of a c.c. so consumed constitutes the blank to be deducted from all tests. Pay no attention should the dark blue of the blank begin to fade in a few minutes. This is caused by the oxidizing action of the nitric acid left in the solution. In actual work containing vanadium, the blue end point does not fade or change so quickly.

Blanks can also be determined by difference, i.e., a known amount of vanadium is added to a plain steel and it is then analyzed for vanadium. Assume, for example, that the value of the sulphate standard is 1 c.c. equals 0.00254 gram vanadium; further, that to 4 or 5 grams of plain steel have been added 30 mgs. of ferro-vanadium containing 38.23 per cent vanadium. This mixture is then analyzed for vanadium and is found to consume 5.3 c.c. of the standard sulphate. Now  $0.3823 \times 30$  equals 11.469 mgs. of vanadium and should require, if there were no blank, 11.469 divided by 2.54 equals 4.51 c.c.; therefore the blank is 5.3 less 4.51 or 0.79 c.c., or the blank to be deducted from all titrations to get the number of c.c. of sulphate consumed by the vanadium alone.

**CHROME VANADIUM STEELS.**

These steels are titrated as given on pages 8, 9, 30, and 31. On page 8 the directions read to completely reduce the chromium in the solution by adding the sulphate standard until the "chrome green no longer grows darker (that is, the green shade no longer gains intensity) and 2 or 3 c.c. more to insure excess." The following example shows how the operator can be

sure that he has an excess of the sulphate and that, therefore, no chromium remains in the chromic acid state which would consume some of the sulphate standard and be counted as vanadium. This example is particularly useful when steels high in vanadium are to be dealt with, i.e., containing from 0.50 to 2.00 per cent vanadium and over:

#### EXAMPLE.

FIRST PART OF THE TITRATION TO OBTAIN THE CHROMIUM. (MADE BEFORE ADDING THE FERRICYANIDE.)

KMnO <sub>4</sub>	Double Sulphate.
21 c.c.	second reading of the burette
<u>9 c.c.</u>	<u>first reading of the burette</u>
12 c.c. (A)	
	97.2 c.c.
	<u>0.2 c.c.</u>
	97.0 c.c.
	<u>12.0 (A)</u>
	85.0 c.c.

$85.0 \times 0.00085 \times 100$  divided by 2 equals 3.61 per cent chromium when 2 grams are taken.

SECOND PART OF THE TITRATION TO OBTAIN THE VANADIUM PERCENTAGE.  
(MADE IMMEDIATELY AFTER ADDING THE FERRICYANIDE INDICATOR.)

*Sulphate used by the vanadium.*

8.2 c.c. second reading of the burette.

1.0 c.c. first reading of the burette.

7.0 c.c. or (B)

0.8 c.c. (blank)

6.2 c.c.  $6.2 \times 0.00254 \times 100$  divided by 2 equals 0.78 per cent V.

(A) should always be several c.c. in excess of (B) to insure no chromium being dragged over into the second part of the titration in the unreduced state and counted as vanadium.

#### THE TITRATION OF CHROME VANADIUM STEELS IN A MANNER SIMILAR TO FERRO-VANADIUM.

In this laboratory these steels are now frequently titrated for vanadium by oxidizing back the vanadium (after the usual excess of the double sulphate has been dropped in the manner just described to reduce both the Cr and V) by adding the permanganate standard until a strong pink is obtained. The solution is then stirred for a half minute vigorously to note if there is a perceptible fading of the permanganate. If there is a

noticeable fading, then more permanganate is added to, again, obtain a strong pink which must show no perceptible change after thirty seconds further stirring. Then the excess of permanganate is slowly, drop by drop, taken up by adding, with prolonged stirring, the sulphate standard until two drops leave only the faintest suggestion of a pink as one looks down through the solution. When the right point is reached, two drops of the permanganate should again give a distinct increase of the pink shade, even after the prescribed amount of stirring. Two drops of the sulphate standard should reduce this pink again to the faint pink. The solution can be thus adjusted back and forth to suit the operator, to a nicety. It is then ready for the addition of the indicator and the final titration to obtain the number of c.c. used by the blank plus the vanadium, or (B).

#### THE DETERMINATION OF THE CHROMIUM VALUE OF THE DOUBLE SULPHATE, AND THE VANADIUM BLANK FOR CHROMIUM VANADIUM STEELS BY MEANS OF A KNOWN MIXTURE.

Suppose the above values are needed for a steel of about 3 or 4 per cent chromium and 0.50 to 1.00 per cent vanadium; then a suitable mixture would be 2 grams of plain carbon steel, free from vanadium, 170 milligrams of c.p. crystals of potassium dichromate and 0.075 gram of ferro-vanadium of 21.8 per cent V. The analytical data obtained in this particular case, after putting the mixture through the regular operations given in the foregoing pages, are found below, together with the calculations:

KMnO<sub>4</sub>, used in the first part  
of the titration to obtain  
the chromium value.

65.8 c.c.
56.2 c.c.
<hr/>
9.6 c.c.

80.6 c.c.
9.6 c.c.
<hr/>
71.0 c.c.

The double sul-  
phate used by the  
chromium, etc.

81.0 c.c.
00.4 c.c.
<hr/>
80.6 c.c.

used by the chromium, alone.

Potassium dichromate contains 35.35 per cent chromium; therefore  $0.170 \times 0.3535$  divided by 71.0 equals 0.00847, or 1 c.c. of the double sulphate equals 0.00847 gram of chromium.

The second part of the titration made immediately after adding the ferricyanide indicator gave the following readings of the sulphate consumed by the vanadic acid in the solution:

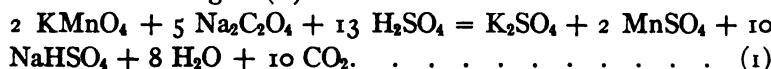
88.2 c.c. second reading of burette.  
81.0 c.c. first reading of burette.  
7.2 c.c. sulphate used by  $V_2O_5$  and the blank.

$0.075 \times 0.218$  equals 0.01635 gram of vanadium added. Taking the vanadium value of the sulphate standard as found by standardizing it against sodium oxalate, as given on page 42, or 1 c.c. equals 0.002536 gram of vanadium, one obtains by dividing the vanadium added, or 0.01635, by 0.002536 a quotient of 6.4; hence 7.2 c.c. minus 6.4 c.c. equals 0.8 c.c. or the sulphate blank to be deducted from the total amount of sulphate consumed in the vanadium titration of the above range of chrome vanadium steels.

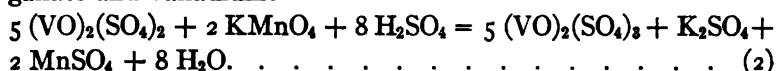
#### THE STANDARDIZATION OF THE DOUBLE SULPHATE FOR VANADIUM BY SODIUM OXALATE.

(A) The strength of the standards per liter are the same as given on page 33. 150 mgs. of c.p. sodium oxalate prepared according to Sorensen are weighed into a beaker, and dissolved in 20 c.c. of 1 : 3 sulphuric acid plus 150 c.c. of distilled water. (This sodium oxalate can be obtained for a small fee from the Bureau of Standards at Washington, D. C., or can be prepared by recrystallizing the c.p. salt offered by the dealers.) The mixture of sodium oxalate is heated to about 80° C. and titrated with the permanganate standard solution until one drop of the same changes the mixture to the faintest pink.

(B) Also a measured amount of the permanganate standard is placed in a beaker together with 20 c.c. of 1 : 3 sulphuric acid and titrated with the double sulphate standard until the pink color just disappears to get the ratio between the two standards. ( $10 FeSO_4 + 2 KMnO_4 + 8 H_2SO_4 = 5 Fe_2(SO_4)_3 + 8H_2O + K_2SO_4 + 2 MnSO_4$ ) The following equation explains the reaction occurring in (A):



Equation (2) shows the relation between potassium permanganate and vanadium:



Equation (1) shows that 2 KMnO<sub>4</sub> are equivalent to 5 Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

Equation (2) shows that 2 KMnO<sub>4</sub> are equivalent to 10 V; therefore

$$5\text{Na}_2\text{C}_2\text{O}_4 \text{ are equivalent to } 10\text{V.} \\ (670) \qquad \qquad \qquad (510)$$

The following proportion will hence give the vanadium equivalent of 0.150 gram of sodium oxalate:

$$670 : 510 :: 0.150 : X. \\ X = 0.11417 \text{ gram of vanadium.}$$

By titration (A) it was found that 45.35 c.c. were required of the permanganate standard to combine with 0.150 gram of oxalate so that 1 c.c. of the permanganate equals 0.11417 divided by 45.35, or 0.002517 gram of vanadium. By titration (B) it was found that 40 c.c. of the sulphate were equivalent to 40.3 of the permanganate; therefore 1 c.c. of the double sulphate equals 0.002517 × 40.3 divided by 40, or 0.002536 gram of vanadium. The double sulphate standard should be tested according to (B) on each occasion that it is used and its vanadium value adjusted according to the relation so found.

#### SOME RECENT ANALYSES OF FERRO-VANADIUM.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	Per cent.				
C.....	0.06	0.05	0.08	0.13	0.19
Mn.....	0.14	0.18	0.19	0.22	4.11
Si.....	1.52	0.97	0.66	0.92	8.35
V.....	40.41	40.54	39.40	39.50	35.62
Ni.....	0.72	1.32	1.68	2.50	7.74
Cu.....	None	None	None	.....	None
Al.....	0.95	1.22	1.33	0.92	1.43
Mo.....	0.92	1.00	0.92	0.60	.....
Fe.....	54.65	54.10	55.20	54.50	42.60
P.....	.....	.....	.....	0.13	.....
S.....	.....	.....	.....	0.65	0.20

For the determination of Vanadium in Vanadium Ores, see page 301.

## CHAPTER III.

### FERRO-TITANIUM AND TITANIUM STEEL.

#### SOLUBLE FERRO-TITANIUM.

\* *Titanium.* When ferro-titanium of low titanium content, 8 per cent titanium for example, dissolves almost completely in sulphuric acid, proceed in the following manner: Dissolve from 0.4 to 0.5 gram of drillings in 30 c.c. 1 : 3 sulphuric acid. Filter and keep the insoluble residue if any. After washing it free from blue iron test with potassium ferricyanide, it is fused with twenty times its weight of sodium carbonate. (Use 1 : 10 sulphuric acid for washing.)

Nearly neutralize the filtrate and washings with 1 : 3 ammonia water. Dilute to 300 c.c. with water. Add to the cold solution 5 grams of sodium thiosulphate † dissolved in water. Boil gently for half an hour, and filter, using paper pulp. Wash with sulphurous acid water (2 c.c. of conc. sulphurous acid to 500 c.c. of water) until no test for iron is obtained. The washed precipitate is ignited and fused with twenty times its weight of sodium carbonate. Keep the fusion molten at a bright red heat for forty minutes. Dissolve in water in a platinum dish; add ashless paper pulp; filter; wash thirty times with sodium carbonate water. Heat the filtrate to boiling in a beaker; add hydrochloric acid drop by drop to the filtrate, and note if a white precipitate forms at any time before the filtrate becomes acid. If a precipitate forms, then roast the sodium titanate to free it from pulp, and fuse again as before; filter; wash; and treat the now aluminum-free titanate as follows:

\* That is, 5 grams of "thio" for every 50 mgs. of Ti likely to be in the solution.

† Read pages 57 to 60.

\* Spread filter and residue in a small dish and cover it with about 30 c.c. of 1 : 3 sulphuric acid. It is heated on a water bath for half an hour, or until all but the filter pulp is in solution. The pulp is filtered out and washed thirty times with dilute 1 : 20 sulphuric acid water and then with water until the washings no longer show a test for sulphuric acid with barium chloride solution. Burn this washed pulp to make sure that all titanate is dissolved. The filtrate and washings are nearly neutralized with ammonia; 5 grams of sodium thiosulphate are added; and the titanic acid is precipitated and washed as before with sulphurous acid wash. It is given forty washings and ignited and weighed as  $TiO_2$  plus a little  $SiO_2$ . The residue is treated with from 5 to 10 drops of conc. sulphuric acid. The crucible is filled about three-fourths full of c.p. hydrofluoric acid and freed from silica as in steels. The weight thus obtained, being the pure  $TiO_2$ , is multiplied by 60.04 and divided by the weight taken for analysis to obtain the percentage of titanium.

The small insoluble residue obtained from the first solution of the drillings in 1 : 3 sulphuric acid is fused with twenty times its weight of sodium carbonate. The melt is dissolved in water; washed thirty times with sodium carbonate water. The filter and residue are spread out in a small dish with 20 c.c. 1 : 3 sulphuric acid and heated on a water bath for thirty minutes to dissolve the titanate of soda. The paper pulp is then removed by filtration, and the filter is washed thirty times with 1 : 20 sulphuric acid. The filtrate and washings from the pulp are made nearly neutral with ammonia water; 5 grams of "thio" are added; and the solution is boiled gently for half an hour. The titanic acid thus obtained is combined with the main precipitate obtained in like manner with sodium thiosulphate. It is roasted with it just before it is fused the first time with sodium carbonate to remove alumina.

\* Or the filter and residue can be roasted; fused with 10 gms. of  $KHSO_4$ ; the melt dissolved; filtered; the filtrate and washings nearly neutralized and the Ti precipitated as before with "thio."

## SULPHUR, PHOSPHORUS AND ALUMINUM \* IN FERRO-TITANIUM.

The sulphur, phosphorus and aluminum in all varieties of ferro-titanium can be best obtained by fusing the drillings or powdered material in a platinum crucible with 20 grams of sodium carbonate ground thoroughly with four grams of potassium nitrate. A double fusion should be made. Fuse one gram of sample as above. When the melt is in a state of quiet fusion, keep it at a bright red heat for 30 minutes longer. Dissolve the fusion in a porcelain or platinum dish in hot water. A platinum dish is best for this work. If the supernatant fluid in the dish is tinged with green, or in high per cents of manganese of 1 per cent and above is a deep green, then add a few drops of absolute alcohol which will convert the green manganate of soda into the brown oxide of manganese. Continue to warm the solution until all green color is gone and the liquid is colorless. This procedure leaves all of the manganese with the iron and titanium. Wash the residue with sodium carbonate water. Roast it; fuse again; dissolve; treat with alcohol; filter; wash and combine the two filtrates and the washings in one beaker. Add to this solution, which contains all of the sulphur, phosphorus and aluminum in the alloy, 1 : 1 hydrochloric acid until the solution is slightly acid. Heat to boiling. Add a slight excess of ammonia which will precipitate all of the aluminum as hydroxide and phosphate. This precipitate, if present in considerable quantity, will carry all of the phosphorus present in the ferro. It is washed with ammonium nitrate water and dissolved off the filter at once with hot 1 : 1 hydrochloric acid. The filter is washed free of acid and should be burned, weighed, and its weight added to the final weight of the  $\text{Al}_2\text{O}_3 + \text{SiO}_2$ .

It is claimed that aluminum precipitated from solutions containing sodium chloride carries with it a certain amount of soda salt that cannot be removed from it by wash water. This is

\* Aluminum can also be obtained as given on page 23, except that the ferro is dissolved in  $\text{H}_2\text{SO}_4$ .

why the aluminum hydroxide is redissolved in 1:1 hydrochloric acid. It is then precipitated hot with ammonia in slight excess and washed with ammonium nitrate water; ignited and weighed, as  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5 + \text{SiO}_2$ . The silica is removed by hydrofluoric acid and a few drops of sulphuric acid as usual, and the residue is ignited and weighed again as  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ . This residue is fused with twenty times its weight of sodium carbonate. The melt is dissolved in water; acidulated with nitric acid in slight excess. The volume is made up to 50 c.c.; boiled with  $\text{KMnO}_4$ ; and the phosphorus precipitated as usual with molybdate solution. The number of milligrams of phosphorus found is calculated to percentage and also to  $\text{P}_2\text{O}_5$ . The milligrams of the latter are deducted from the weight of  $\text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$  and the remainder is multiplied by 53.03 and divided by the weight taken for analysis to obtain the percentage of aluminum in the alloy. (See page 332, Phosphorus in Graphite.)

If the original filtrates from the double fusion show very little or no aluminum on being treated with hydrochloric acid until the hot solution is only faintly alkaline, then there is a possibility that the filtrate from this aluminum may still contain phosphorus. To obtain this phosphorus a solution of ferric chloride free of phosphorus and sulphur is added to the filtrate from the small quantity of aluminum or to the slightly acid solution, if no aluminum hydroxide formed.

This solution, which should be faintly colored with ferric chloride and slightly acid, is precipitated hot with a small excess of ammonia. The precipitate is filtered out; washed with hot water; is dissolved off the filter with a little hot 1.20 nitric acid. The filter is washed free of iron test, using potassium sulphocyanate for the detection of iron in the washings. The dilute nitric acid wash water is used. (See Phosphorus in Steel, page 257.) Concentrate the filtrate and washings to 40 c.c. Boil with a little permanganate; clear with ferrous sulphate; and finish as in steels. The phosphorus found in the iron precipitate plus that found with the aluminum hydroxide, if any formed, equals the total phosphorus in the ferro.

The filtrate from the aluminum hydroxide, or iron hydroxide, or both, is made slightly acid with hydrochloric acid and evaporated to dryness in a 600 c.c. casserole. Ten c.c. of 1 : 1 hydrochloric acid are added to the dry residue. It is heated with a cover on the dish; 200 c.c. of water are added; and the dish is heated nearly to boiling, or until all of the salt is dissolved. The solution is filtered. The filter is washed with 1 : 10 hydrochloric acid. The filtrate and washings are precipitated with 20 c.c. of a saturated solution of barium chloride. The barium sulphate formed is allowed to settle twelve hours. It is filtered with a little pulp; washed free from chloride tests with water only; burned in a weighed platinum crucible; moistened with a drop or two of 1 : 3 sulphuric acid, as the burning of the paper always reduces a little of the barium sulphate to BaSO<sub>3</sub>. It is ignited again and weighed as BaSO<sub>4</sub>, which weight, multiplied by 13.73 and divided by the weight taken for analysis, gives the percentage of sulphur in the sample. Deduct a blank due to the fluxes and acids used. Blanks should always be made, as sodium carbonate and acids are liable to contain sulphates, iron and aluminum.

#### IRON IN SOLUBLE FERRO-TITANIUM.

Dissolve 0.5 gram of sample in 1 : 3 sulphuric acid. If there be any insoluble residue that is not white, filter the same out and wash it with dilute sulphuric acid. Roast it. Fuse it with potassium bisulphate. Dissolve the melt in dilute sulphuric acid and add it to the filtrate and washings from the insoluble residue. Dilute the slightly acid filtrate and washings to 200 c.c. Pass hydrogen sulphide through the same until the iron is entirely reduced. It will be colorless when hot. The reduction will take about an hour, with the gas passing at a rather rapid rate. Filter the solution into an 800 c.c. boiling flask. Wash the filter with 1 : 10 sulphuric acid until free of iron test.\* Pass

\* The residue on this filter will contain all of the copper present which can be roasted and finished as in steels for Cu.

hydrogen sulphide through this filtrate for one hour more. (Saturate the acid wash with H<sub>2</sub>S before using.)

Now pass a stream of carbon dioxide through the solution, keeping the same at boiling temperature during the time that the CO<sub>2</sub> is passing. When a piece of filter paper, moistened with a water solution of lead acetate, is no longer discolored, even slightly, when held in the neck of the flask, the excess of hydrogen sulphide is all driven out. Place the flask in cold water with the stream of carbon dioxide still passing through it. The glass tube that carries the H<sub>2</sub>S and CO<sub>2</sub> into the fluid should, of course, reach nearly to the bottom of the boiling flask. When the contents of the flask are cold, titrate with standard permanganate of potash until one or two drops yield a pink color that is permanent for several minutes. The same standard that is used for titrating iron in ferro-vanadium can be utilized in this determination. One c.c. of the standard equals 0.00556 gram of metallic iron.

#### MANGANESE IN FERRO-TITANIUM SOLUBLE IN SULPHURIC ACID.

Dissolve 0.100 gram in 10 c.c. 1 : 3 sulphuric acid. Add 10 c.c. concentrated nitric acid. Boil off red fumes. Dilute to 35 c.c. with water and finish as in steels. This applies to manganese not in excess of 1 per cent. Use 0.05 gram for manganese content exceeding 1 per cent. Accurate to 2 per cent Mn. For higher percentages of manganese dissolve 1 gram of sample in 30 c.c. 1 : 3 sulphuric acid.\* Oxidize by boiling with 10 c.c. conc. nitric acid and 1 gram of potassium chlorate. Add 60 c.c. 1 : 3 sulphuric acid and evaporate to thick fumes. Cool, add water and heat until all is dissolved except perhaps some of the titanic oxide and silicic acid. Be sure that all iron and manganese sulphates are in solution. Wash the cold solution into a liter flask. Fill the flask one-half full with distilled water. Add a rather thick paste of manganese-free zinc oxide

\* One can also finish from this stage on as directed on page 278 by the author's method for manganese above 2 per cent.

and distilled water. Continue the addition of the zinc oxide until the iron and titanium settle out well, avoiding any unnecessary excess of the zinc oxide. Cool, if necessary, to the temperature of the room, and dilute the contents to the liter mark with distilled water. Mix ten times, inverting the stoppered flask each time.

Permit the precipitate to settle for a half-hour with the flask in an inclined position. Pour the supernatant fluid through a large, dry filter into a dry beaker. Use two filters to hasten matters. Rinse a hundred c.c. pipette three times with portions of the filtrate. Then draw out a 300 c.c. portion and a 400 c.c. portion. Place these in separate boiling flasks, labeling them 300/1000 and 400/1000, respectively. Add two drops of 1.20 nitric acid to each of these aliquot parts. Heat the 300 c.c. to boiling, and titrate with standard permanganate of potassium, adding a little at a time. Shake thoroughly with each addition of the permanganate solution, reheating the solution between times. When three drops finally produce a slight but distinct pink color in the hot supernatant fluid, after a reheating and thorough shaking, the end point is reached. Deduct 0.2 c.c. from the total permanganate used. Multiply its value per c.c. in milligrams of iron by 0.2945 to find its value in milligrams of manganese.\*

Titrate the 400 c.c. part in like manner and average the two results, calculating them as 3/10 and 4/10 of a gram, respectively. (See also Mn in Insoluble Ferro-Titanium.)

#### STANDARDIZATION OF THE PERMANGANATE SOLUTION FOR IRON AND MANGANESE.

Weigh 3.16 grams of c.p. potassium permanganate crystals into a liter flask. Dissolve in distilled water and dilute to liter mark.

Weigh 0.2850 gram of c.p. recrystallized oxalic acid into a 200 c.c. beaker. Dissolve the crystals in 100 c.c. of hot water.

\* The following reaction shows how Volhard's method proceeds:  $3 \text{MnSO}_4 + 2 \text{KMnO}_4 + 2 \text{ZnO} = \text{K}_2\text{SO}_4 + 5 \text{MnO}_2 + 2 \text{ZnSO}_4$ .

Add 30 c.c. 1 : 3 sulphuric acid and titrate this hot solution with the permanganate solution. This latter should not be standardized for, at least, twelve hours after it has been dissolved and made up to 1 liter.

This amount of oxalic acid will require usually 45.50 c.c. of permanganate of the above strength to render it a faint pink that is permanent for several minutes. As the oxalic value of a permanganate solution multiplied by 8/9 gives its iron value therefore the latter is found by this calculation:  $0.2850 \div 45.50 \times 8/9 = 0.005567$ , or 1 c.c. of the permanganate equals 0.005567 gram of metallic iron. This value multiplied by 0.2945 yields the value of the same solution in grams of manganese, or  $0.005567 \times 0.2945 = 0.001639$  gram of manganese. For check 0.280 gram oxalic acid took 44.8 c.c. KMnO<sub>4</sub>, or  $0.280 \div 44.8 \times 8/9 = 0.005555$  and  $0.005555 \times 0.2945 = 0.001636$ , or 1 c.c. = 0.001636 gram of manganese. Average iron value equals 0.00556 gram and average manganese value equals 0.001637 gram per c.c. Compare the theoretical factor for manganese with that found by standardizing the permanganate standard by putting a ferro-manganese, containing a known per cent of manganese, through the identical process of fusion with bisulphate; precipitation with zinc oxide, etc. (See Analysis of Ferro-Manganese, page 188.)

#### SILICON IN SOLUBLE FERRO-TITANIUM.

Dissolve 1 or 2 grams of drillings as in steels. Evaporate to fumes of sulphuric acid. Dissolve in water. Filter, wash, ignite, weigh, evaporate with a few drops of conc. sulphuric acid, and the usual amount of hydrofluoric acid. Ignite and calculate the loss of weight as silicon. Should a white coating appear on the lid of the crucible when the sulphuric acid is being driven off, it means that there has not been a sufficient amount of sulphuric acid added, some of the titanium having volatilized as fluoride.

In such event, repeat the analysis, using a little more sulphuric acid with the hydrofluoric acid.

**NICKEL, VANADIUM AND CHROMIUM.**

These elements are determined in soluble ferro-titanium as in V, Ni and Cr steels. See pages 7, 30, 31 and 39. Mix considerable washed asbestos pulp with the slimy mixture of silicic and titanic acids before filtering out the excess of manganese oxide, in the Cr and V determinations. Add paper pulp and filter off the titanic acid, etc., before adding the citric acid, in the Ni analysis.

**CARBON IN SOLUBLE FERRO-TITANIUM.**

Some ferro-titaniums of low silicon content can be completely decarbonized at 950° C. in a fused silica tube with oxygen. See Electric Combustion Furnace, page 224. It is safer to burn the sample in red lead. Burn 1 or 2 grams of thin drillings or 30-mesh powder with 4 grams of red lead.

**INSOLUBLE FERRO-TITANIUM.**

Carbon, sulphur and phosphorus are determined as given in the analysis of soluble ferro-titanium.

**SILICON AND TITANIUM.**

These elements are best separated by fusion of 0.5 gram of the finely ground substance with 15 grams of acid potassium sulphate in a 40 c.c. platinum crucible. This fusion is highly satisfactory if conducted with a little experience. Heat the crucible very gradually at first, using the white flame of an argand burner. Keep the melt below redness until all of the water has been driven out of the flux without sputtering. When slight fumes of sulphuric anhydride begin to make their appearance the heat can be increased to low redness. Maintain this temperature until the substance is in a state of clear fusion, and is a pure yellow, free of all black specks.

If the argand burner flame is properly adjusted, this operation can be going on with only occasional attention. When all black is gone, raise the heat until fumes of sulphuric anhydride come off briskly when the lid is lifted slightly.

Then turn off the heat and run the melt well up the sides. Place the crucible in a 250 c.c. casserole with 50 c.c. of water plus 50 c.c. of 1 : 3 sulphuric acid. Dissolve with heat. Filter out the white insoluble residue; wash it free of iron and sulphate, using barium chloride solution for the latter tests and KCNS for the former. Ignite it in a weighed crucible. Weigh as  $\text{SiO}_2$  plus a little  $\text{TiO}_2$ . Evaporate with HFl and a few drops of  $\text{H}_2\text{SO}_4$  and calculate the loss of weight to silicon. Keep the non-volatile portion to add to the main portion of  $\text{TiO}_2$ .

The filtrate and washings from the silica are made nearly neutral with ammonia and precipitated with thiosulphate of soda, and finished as in soluble ferro-titanium for Ti.

#### IRON.

Fuse 0.5 gram as for silicon. Reduce with  $\text{H}_2\text{S}$  and finish as given under the soluble ferro.

#### ALUMINUM.

Proceed by fusion as given under aluminum in soluble ferro-titanium.

#### MANGANESE IN INSOLUBLE FERRO-TITANIUM.

If the percentage of manganese is under two per cent, fuse 0.100 or 0.05 gram with twenty times this weight of sodium carbonate and one-fifth that amount of potassium nitrate. Dissolve the melt in a small porcelain dish with as little water as possible. Clean the platinum crucible with a little hydrochloric acid; acidulate the water solution of the melt with the same acid. Add to this solution the cleanings of the crucible and also 10 c.c. of 1 : 1 sulphuric acid. Evaporate to thick fumes. Dissolve the residue in water. When the iron sulphate is dissolved, wash the solution into a 10 by 1 inch test tube and dilute to 20 c.c. Add 10 c.c. of conc. nitric acid and finish as in steels.

For higher percentages of manganese proceed as given for high manganese in soluble ferro-titanium except that the

substance is gotten into solution by a bisulphate fusion as given under the determination of silicon in insoluble ferro-titanium. Transfer the sulphuric acid solution of the melt to a liter flask and precipitate the iron and titanium with zinc oxide. Use 1 gram of sample and fuse it with 30 grams of bisulphate.

#### TITANIUM STEELS.

For phosphorus, manganese, silicon, aluminum and carbon proceed as in plain steels if the titanium is present to the extent of a few tenths of a per cent.

#### SULPHUR.

Even a few tenths of a per cent of titanium lead to low sulphur results by the evolution process. For example, where results showing 0.006 per cent by evolution were obtained, 0.012 sulphur was gotten by the ordinary gravimetric sulphur method for steels. Again, 0.075 per cent sulphur was gotten by evolution in a titanium experimental ingot when the gravimetric result was 0.11 per cent. Use either the gravimetric process by direct solution, or fuse 2 grams of sample with 20 grams of sodium carbonate plus 4 grams of niter, and proceed as in sulphur in high silicon ferro-vanadium, filtering out the sodium titanate before acidulating with HCl.

#### TITANIUM IN STEEL.

##### *Gravimetric.*

The titanium is determined gravimetrically as in soluble ferro-titanium except that four or five grams of sample should be used.

##### VOLUMETRIC.

So far the most practical way is the well-known color method, using hydrogen peroxide. The author proceeds as follows:

Determine gravimetrically the amount of titanium in a ferro-titanium containing from about 8 to 10 per cent of titanium, for use as a color standard.

#### PLAIN TITANIUM STEEL.

If the titanium content is 0.05 per cent or over, weigh 0.500 gram of drillings into a 10 by 1 inch tube. Also weigh 0.500 gram of a plain carbon steel that contains no titanium by the qualitative test. Add to the latter enough of the standard ferro-titanium to bring the amount of titanium present in this standard mixture to within about 0.05 per cent of the titanium content of the test. If the test is likely to be about 0.15 per cent Ti, then the standard should either be about 0.10 per cent Ti or 0.20 per cent Ti. The nearer the standard is to the test, in titanium content, the better.

Dissolve the drillings in 10 c.c. of dilute sulphuric acid.\* Add 5 c.c. of conc. nitric acid and boil off red fumes. Cool, rinse the standard into a glass-stoppered comparison tube of about 15 to 16 mm. outside diameter and with the graduated part about 38 cm. long. Add to the solution in the comparison tube 5 or 6 c.c. of the peroxide mixture used in qualitative Ti and V tests, page 5. Stopper the tube and mix the contents thoroughly. Transfer the test to the other comparison tube and treat it in like manner. If there is a great difference in color between standard and test, results will only be roughly approximate and the work should be repeated, preparing a new mixture of standard ferro-titanium and plain carbon steel, to imitate the test within the 0.05 limit or closer.

The following actual case will illustrate calculations, etc.:

The standard mixture consisted of 8 mg. of 8 per cent Ti ferro plus 500 mg. of a plain carbon steel of approximately the same carbon content as the sample to be tested.

The test matched the standard at 38.3 c.c. with the standard diluted to 35 c.c. Since the standard contained 8 mg. of 8 per cent ferro-titanium, its color was due to the presence of 0.008 X

\* Warm in boiling water before adding the nitric acid until the solution is as free as possible of black scum, or the nitric acid will dissolve the scum to a brown color which will augment the similar color due to the titanium and peroxide. Select a plain carbon steel as near the carbon content of the titanium steel as possible to reduce the interference due to the color of the dissolved carbon to a minimum. See page 60.

0.08, or 0.00064 gram, of metallic titanium; therefore we have the proportion:

$$\begin{array}{lll} \text{Stand. Vol.} & & \text{Test Vol.} \\ 35 \text{ c.c.} & : & 38.3 \text{ c.c.} \end{array} :: 0.00064 : X,$$

or  $38.3 \times 0.00064 \div 35 = 0.0007$ , or 0.0007, gram of titanium found.  $0.0007 \times 100 \div 0.5 = 0.14$ , or 0.14 per cent titanium when 0.5 gram is taken for analysis. The gravimetric result on this sample was 0.158. Another sample gave 0.134 per cent by color and 0.140 per cent by gravimetric analysis.

For percentages as low as 0.05 per cent and under, use a gram of sample and proceed accordingly, preparing standard mixtures of similar percentage. If the titanium steel also contains not over one-half per cent of elements that color acid solutions, such as chromium and nickel, the amounts of the latter present in the test should be determined by the rapid methods given under chromium and nickel in steel. Add to the standard enough shot nickel if titanium nickel steel is being tested, or enough potassium dichromate reduced with the least possible excess of sulphurous acid if the test be chrome-titanium steel, to exactly imitate the sample under examination, and then proceed as usual.

If the steel contains several per cents of chromium,\* fuse 2 grams with a mixture of 20 grams of sodium carbonate and 4 grams of niter. Dissolve the melt in water. Filter; wash the residue on the filter with sodium carbonate water. Roast the pulp out and fuse again as before. Dissolve in water, filter and wash. Then dissolve the residue off the filter with hot hydrochloric acid. Wash the filter free of iron test. Dilute the filtrate and washings to 300 c.c. and pass  $H_2S$  through it until all platinum has been precipitated. Filter; wash the sulphides with  $H_2S$  water. Evaporate the filtrate and washings to 10 c.c., adding one gram of potassium chlorate before beginning the evaporation, to oxidize the iron and remove  $H_2S$ .

Add at this stage 30 c.c. 1 : 3 sulphuric acid and evaporate to heavy fumes. Dilute with water and then finish exactly as in

\* Read pages 62 and 63.

the gravimetric determination of titanium in plain carbon steels.

The color method might also be applied to such steels by first removing the chromium by a sodium carbonate and niter fusion as just given, using 0.500 gram of sample. The sodium titanate and oxide of iron could then be spread, filter and all, in a small porcelain dish with 30 c.c. 1 : 1 hydrochloric acid and heated for 30 minutes or more. The pulp could be filtered out and washed; 30 c.c. of 1 : 3 sulphuric acid added; the filtrate and washings evaporated to thick fumes; transferred to a 10 by 1 inch test tube; boiled with 5 c.c. conc. nitric acid and finished by color. For a standard add to a plain chromium steel a suitable amount of ferro-titanium and fuse with sodium carbonate and niter, putting the fusion, etc., through exactly as the test. Use this for the color standard. Or after removal of the chromium and vanadium by a double fusion with sodium carbonate and niter, then fuse the iron oxide and sodium titanate with potassium bisulphate and finish by color, or gravimetrically.

#### VANADIUM-TITANIUM STEEL.

Remove the vanadium by fusion as in removal of chromium. Then finish gravimetrically as given under chromium titanium steel, or convert into sulphate; evaporate to 10 c.c.; wash into a 10 by 1 inch test tube; boil with 5 c.c. conc. nitric acid, and finish by color.\*

#### QUALITATIVE TEST FOR TITANIUM.

Proceed as given under Qualitative Test for Vanadium, page 5.

#### ANALYSES.

Insoluble ferro-titanium.	Per cent.	Soluble ferro-titanium.	Per cent.
Titanium } Ti <sub>2</sub> O <sub>3</sub> .....	87.80	Titanium.....	8.12
Oxide.....		Manganese.....	0.58
Silica SiO <sub>2</sub> .....	0.85	Silicon.....	0.50
Iron Oxide Fe <sub>2</sub> O <sub>3</sub> .....	4.64	Iron.....	86.92
Sulphur.....	0.52	Aluminum.....	3.00
Carbon.....	1.89	Phosphorus.....	0.10
Phosphorus.....	0.055	Carbon.....	0.26

\* Read pages 62 to 63.

**SOLUBLE FERRO-TITANIUM, ELIMINATING SOME OF THE  
FUSIONS.**

*Titanium.* To avoid as much as possible the making of fusions the author now analyzes ferro-titanium of the soluble type as follows: Dissolve 1 gram of the drillings, or powder, in a liter boiling flask in 50 c.c. of 1 : 3 sulphuric acid, heating until action is over. Carry along a test mixture of about the same proportions. For example, 30 mg. of metallic aluminum and 0.850 gram of plain carbon steel will usually come within close range; or still better a ferro-titanium of known Al and Ti content can be analyzed at the same time to test the accuracy of the operator's manipulations.

Dilute the above solution to 300 c.c. and peroxidize it in the manner described on page 23, beginning at the point where one is directed to "dilute to about 300 c.c.," obtaining filtrates A and B. If on dissolving the iron off the filter, a reddish, rouge-like portion of the iron resists the action of the hot 1 : 1 HCl, remaining as a red stain on the paper pulp, then wash the latter with water until the washings no longer give a test with silver nitrate; burn the pulp in a platinum crucible and fuse it at a bright red heat with the sodium carbonate for a half hour, using enough of the flux to equal about twenty times the weight of the ash. Dissolve the fusion in water; acidulate with HCl, heating with enough of the latter to dissolve all of the iron; add this solution to the main iron solution and proceed with the second peroxidation. If the ferro contains as much as 10 per cent Al, a third solution, peroxidation and filtration are necessary obtaining a third filtrate and washings. The combined three filtrates will contain all of the Al in the ferro-titanium. If any vanadium be present it will all be in the same place. All of the iron and titanium will be on the filter from the third peroxidation and also a little of the iron will remain as a film on the inside of the boiling flask. The film can be removed by warming in the flask a little of the 1 : 1 HCl that is to be used to dissolve the main iron and titanium off the filter. Wash the fil-

ter and pulp from the final solution of the iron and titanium, until it tests free of iron with KCNS solution. Retain the filter and pulp and use it to catch the first precipitation of the titanium, or ignite it along with the titanium as it may retain some of the Ti.

The final solution of the iron and titanium in HCl, being now free of Cr, V and Al, is taken to heavy fumes with 50 c.c. of 1 : 3 sulphuric acid; cooled; and dissolved to a clear solution with 100 c.c. of water. Filter out any white insoluble matter; wash it free of iron test with 1 : 40 H<sub>2</sub>SO<sub>4</sub>; neutralize the filtrate and washings with 1 : 3 ammonia, adding the same until a slight turbidity is obtained that will not dissolve on continued stirring; add three drops of 1 : 3 H<sub>2</sub>SO<sub>4</sub>; and then add 10 grams of sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>). Boil thirty minutes, slowly; add some ashless paper pulp, filter and wash with sulphurous acid water (500 c.c. of water to which has been added 5 c.c. of H<sub>2</sub>SO<sub>3</sub>); after fifteen washings, begin to test the wash water for iron and continue the washing until no blue test for iron is obtained with potassium ferricyanide. Dry the filter and pulp, and burn it at a low heat until the paper is all gone; if the residue in the crucible is not pure white or slightly yellow, but has a reddish tint, it still contains iron and must be fused with 10 grams of acid potassium sulphate (KHSO<sub>4</sub>). This fusion is very satisfactory but must not be hurried. Place the 10 grams of KHSO<sub>4</sub> in the crucible on top of the residue; cover the crucible and *warm* it over an argand burner, cautiously; lift up the lid occasionally to make sure that the heat is not high enough to cause the flux to spatter against the lid; continue this low heat for a half hour or more until, on increasing the heat a little, there arises a slight fume of sulphuric anhydride; continue to increase the heat slightly until, finally, a bright red heat has been attained without any boiling action. The melt should be transparent and contain no undissolved dark particles; it should be as clear as water, when red hot, except for white flakes of silica if the latter be present. Place the melt, crucible and all, in a No. 5 porcelain dish together with 50 c.c. of 1 : 3 H<sub>2</sub>SO<sub>4</sub> and an equal amount of water, and heat

until the melt is all dissolved out to a clear solution with perhaps some white particles of silica floating in it. Do not filter, but neutralize the acid until a faint white cloudiness is obtained that will not dissolve on persistent stirring; reprecipitate the titanium as before by boiling with 10 grams of the thiosulphate; filter and wash the precipitated titanium as before; dry it; ignite and weigh it as titanic oxide plus some  $\text{SiO}_2$ ; remove the latter as described on page 44.

*Aluminum.* This element can be obtained from the combined filtrates from the peroxidations, page 57, by acidulating the same with HCl and precipitating the Al with a slight excess of ammonia after boiling off the carbon dioxide. This Al should be redissolved in HCl and reprecipitated to free it from sodium salt. It is then ignited and weighed as described on page 46, except that any phosphorus that may be found in the precipitate cannot be taken as the total P in the ferro since by dissolving the latter in sulphuric acid much of the P is lost as phosphine. Deduct from the Al found, the *excess* of Al gotten in the test mixture, if any, over and above the Al put in the test mixture.

*Phosphorus and Sulphur.* These elements can be best determined as given on page 45, but if it is desired to avoid niter and carbonate fusions in platinum, then fuse 1 gram of the finely powdered sample, or thin drillings, in an iron crucible with 8 grams of sodium peroxide; dissolve the fusion out in water in the same manner as described for chrome ore on page 140; remove the crucible and acidulate the water solution with HCl; heat until the iron is all dissolved; precipitate the iron out with ammonia; dissolve it off the filter with 1.20 nitric acid and finish for phosphorus by boiling with a slight excess of  $\text{KMnO}_4$ , clearing with ferrous sulphate and precipitating with molybdate. Run blanks on all operations for phosphorus.

*Iron.* The iron can be obtained as given on page 47, or 0.500 gram of the sample can be decomposed as described for titanium on page 60 up to the point where all is in solution and ready for the second peroxidation; evaporate this iron-titanium solution to 250 c.c.; reduce it with stannous chloride; take up the

excess of the latter with mercuric chloride; and titrate the iron with a standard solution of potassium dichromate as in iron ore.

*Insoluble Ferro-Titanium.* Instead of decomposing this type of ferro-titanium by the bisulphate fusion as outlined on page 51, 1 gram of the finely ground sample can be fused in a platinum crucible with a mixture of 10 grams of sodium carbonate and 2 grams of niter. The melt is dissolved out in a platinum dish with water and is then transferred to a casserole *before acidulating* the water solution. An excess of HCl is then added to the water solution. The crucible is rinsed off with water into the casserole; cleaned by warming in it a little HCl. The cleanings are added to the acidulated solution in the casserole which is heated with a cover on it until all action is over. The contents of the casserole are evaporated twice to dryness; dissolved in HCl; heated with 100 c.c. of water; filtered and washed after each evaporation; the combined filters from the two evaporation will contain all of the silica and a little of the titanium; these are ashed carefully; weighed and evaporated with HFL and 5 drops of conc.  $H_2SO_4$ , and the silica obtained from the loss of weight. The residue remaining in the crucible is fused with 20 times its weight of  $Na_2CO_3$ ; dissolved in HCl and added to the filtrate from the second evaporation to dryness to remove silicon. This filtrate and washings now contain *all* of the Ti, P, Al, Fe, and S in the sample. The filtrate can be diluted to a definite volume and one-half reduced with stannous chloride and titrated with standard dichromate solution for iron, paying no attention to the Ti present as Ti has no effect on the dichromate. The other half can be then peroxidized as given on pages 57 and 58 to obtain the other elements. This scheme obtains the iron avoiding the reduction with  $H_2S$ .

#### THE DETERMINATION OF VERY LOW PERCENTAGES OF TITANIUM IN STEEL.

By the scheme given on page 54, a little scum of carbon remains after the solution in sulphuric acid and is dissolved subsequently by the nitric acid, imparting a slight brown color to the solu-

tion. Hence it is, at all times, advisable when preparing a standard mixture to select a titanium-free steel as near to the carbon content of the sample to be tested as possible. In this way about the same amount of color due to the carbon may be in both standard and test. It is necessary to eliminate this color, entirely, when one is to determine the titanium in a sample containing only 0.01 to 0.05 per cent Ti.

Dissolve 4 grams of drillings in 50 c.c. of 1 : 3 sulphuric acid and evaporate to fumes; dissolve by heating with 100 c.c. of water; filter when all iron is dissolved; the residue on the filter, after washing it free of iron test with 1 : 40  $H_2SO_4$ , is ignited in a platinum crucible; evaporated with Hf and a few drops of sulphuric acid. Hold this residue in the crucible and call it B. Add ammonia to the filtrate and washings from B until a slight turbidity is obtained that will not dissolve even with persistent stirring; then add 10 grams of sodium thiosulphate and boil for 30 minutes; filter out the precipitate and wash it with sulphurous acid water and burn it with B. Fuse the total ash with 20 times its weight of  $KHSO_4$ ; dissolve the fusion in water; add to the water solution 100 c.c. of 1.20 nitric acid; heat; cool; wash into a 250 c.c. flask; dilute to the mark; mix well and compare with a standard mixture consisting of 5 mgs. of 8.2 per cent ferro-titanium and 4 grams of steel, free of titanium, which has been put through all of the above operations and also diluted to the mark in a 250 c.c. volumetric flask. Suppose that 25 c.c. of the test solution is compared with 25 c.c. of the standard mixture as given on page 54 and that the standard matched the test with the former at 54 c.c. and the latter at 32 c.c. 25 c.c. of the standard equals  $25/250$  of 5 mgs.  $\times$  0.082, or 0.041 mg. Ti; therefore  $54 : 32 :: 0.041$  mg. :  $x$  equals 0.024 mg. Ti in 500 mgs. of sample. 0.024 divided by  $500 \times 100$  equals 0.0048, or per cent Ti in the sample equals 0.0048 per cent.

**THE DETERMINATION OF TITANIUM IN NICKEL STEEL.**

Suppose it is required to obtain the titanium content of a steel containing 3.60 per cent Ni: Dissolve 5 grams of the sample, as on page 54, using 75 c.c. of 1 : 3 sulphuric acid for the solution, heating in boiling water for one hour to eliminate as much as possible the carbon before adding the 25 c.c. of conc. nitric acid to accomplish the oxidation of the iron and dissolve the titanium. For a standard mixture dissolve and oxidize 5 grams of plain steel to which enough nickel ammonium sulphate has been added to equal 3.60 per cent Ni in 5 grams, and also 5 mgs. of 8.20 per cent Ti ferro-titanium. Dilute the cooled solutions of the standard and test to the mark in 250 c.c. volumetric flasks; mix and note if the two solutions are about the same shade of brown. If the standard solution is distinctly browner prepare a new standard using a lower carbon plain carbon steel, adding the nickel sulphate and 5 mgs. standard ferro-titanium. If now there is only a slight difference in the color of the solutions due to dissolved carbon proceed with the comparisons in the manner described on page 54 using 25 c.c. from each flask. This method was used on a steel that contained 0.008 per cent Ti. There would seem to be no objection to using the first method given for very low percentage titanium steels on this almost equally low titanium-nickel steel, in case the operator cannot eliminate the interference of carbon by selection. (See page 60.)

**THE DETERMINATION OF TITANIUM IN CHROMIUM-VANADIUM-NICKEL-TITANIUM-TUNGSTEN STEEL.**

Owing to the interference of the vanadium and the chromium, the latter must be removed. This can be best done by peroxidizing the solution of the sample and standard mixtures in the same manner as described on pages 57 to 58. If the chromium is considerable it will require three peroxidations at least to

remove the chromium and vanadium. The redissolving and reperoxidizing must be continued until the filtrate from the iron and titanium is no longer colored yellow. The steel and standard mixtures are dissolved in 50 c.c. of 1 : 3 sulphuric acid; 0.500 gram of sample is taken for analysis. A chromium-tungsten-vanadium steel containing no nickel or titanium was used as a basis of a standard, and to it was added 35 mgs. of nickel ammonium sulphate and 5 mgs. of 8.20 per cent (Ti) ferro-titanium. After the chromium color has been removed by several peroxidations from the standard and test, the iron and titanium are dissolved off the filters with 50 c.c. of hot 1 : 1 HCl; the filter is washed free of iron; the filtrate and washings will contain all of the titanium and iron except a slight amount that may still remain on the filter, which is ashed and fused with one gram of sodium carbonate; the fusion is dissolved in 20 c.c. of 1 : 1 HCl and added to the main solution of the iron and titanium. Evaporate this latter solution to 5 or 10 c.c.; add 100 c.c. of strong nitric acid; heat with the cover on until all spraying is over and then evaporate to 5 c.c.; add 10 c.c. of water and filter into the comparison tube washing with 1.20 nitric acid; add 10 c.c. of peroxide solution and compare. Example: Test matched the standard mixture as follows: 76.7 c.c. test equal 91.2 c.c. of standard; therefore since the standard contained 0.41 mg. Ti,  $76.7 : 91.2 :: x : 0.41$  mg. Ti, or 76.7 times 0.41 mg. Ti divided by 91.2 divided by 500 multiplied by 100 equals 0.068 per cent Ti. A duplicate analysis on this steel gave 0.070 per cent Ti, using 0.600 gram of sample. In the case of a similar steel that contained 0.80 per cent Ti, the nitric acid solutions containing the iron and titanium, freed as above from the V and Cr, were diluted to 250 c.c. and 50 c.c. were taken from the standard and test for the comparisons. 0.81 per cent Ti was obtained and a check of 0.78 per cent Ti. No attention is paid to the tungsten as it is removed along with the Cr and V.

## CALCULATIONS.

70 mg. of 8.2 per cent Ti ferro-titanium were used in the standard mixture; 61.5 c.c. of standard equal 78 c.c. of test. One-fifth of 70 mg. times 0.082 equals 1.148 mg. Ti. Therefore  $61.5 : 78 :: 1.148 : x$ ;  $x$  equals 1.456 mg. Ti. Now 0.9 gram was taken in this case for the analysis and one-fifth or 0.18 gram of the test was used in the comparison; hence  $0.00145 \text{ gram} \times 100 \text{ divided by } 0.18$  equals 0.809 per cent Ti.

## SOME FURTHER ANALYSES OF FERRO-TITANIUM.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	Per cent.				
Carbon.....	7.00	1.05	0.04	3.69	1.85
Manganese.....	0.28	0.40	0.39	0.19	0.15
Silicon.....	1.08	0.64	2.51	0.42	14.90
Titanium.....	7.30	8.40	20.44	29.17	6.15
Aluminum.....	0.42	2.93	3.10	9.87	2.25
Iron.....	84.20	86.53	73.17	56.78	74.60
Chromium.....			0.52		
Phosphorus.....					0.15

*Chromium.* The chromium was obtained in the above No. 3 as in a steel, no attention being paid to the presence of titanium.

*Analysis of Basic Slag Containing Titanium.*

*Silica.* Dissolve 1 gram of the finely ground slag, after first stirring it into a thin, smooth paste with a very little water, in a No. 5 porcelain dish in 50 c.c. of conc. HCl. Warm until solution is practically complete, evaporate to dryness and heat until very little acid can be detected when hot. Dissolve again in 30 c.c. of conc. HCl.; add 100 c.c. of water; filter; wash free of iron test. Burn in a weighed platinum crucible; add a large excess of  $\text{H}_2\text{SO}_4$ , about 2 c.c. to prevent loss of Ti as fluoride and remove the silica with 15 c.c. of HfI; calculate the loss of weight to silica. For extreme accuracy the solution of the slag should be evaporated twice to dryness with HCl, filtering after each evaporation and solution in HCl and water.

*Oxide of Iron.* Dissolve 1 gram of the slag, as for the silica, in a 600 c.c. beaker and dilute the solution to 300 c.c.; heat to

boiling; reduce with stannous chloride without separating the titanium; cool; add an excess of mercuric chloride solution and titrate with N/20 potassium dichromate as in iron ores.

*Titanium Oxide.* Dissolve 1 gram, as for silica, in a liter boiling flask and dilute to 300 c.c.; make two peroxidations as described on page 57, obtaining the titanium and iron on the filter and the alumina in the combined filtrates and washings from the two peroxidations.

*Oxides of Manganese, Calcium and Magnesium.* Dissolve 1 gram in 50 c.c. of conc. HCl in a 600 c.c. beaker and make two basic separations, as directed for the separation of iron from manganese on page 188, beginning at the point where the filtrate and washings are diluted to 300 c.c. The combined filtrates from the two basic acetate separations contain all the Ca, Mg and Mn in the slag. Acidulate the combined filtrates with HCl and evaporate them, if necessary, to 400 c.c. and make the same slightly but distinctly ammoniacal. Then add slowly a water solution of potassium ferricyanide; use the c.p salt of a clear resinous red color and free of the suggestion of bluish color, as ferricyanide containing blue material is partly decomposed as follows:  $\text{Fe}(\text{CN})_3 \cdot 3 \text{KCN} = \text{Fe}(\text{CN})_2 + \text{CN} + 3 \text{KCN}$ , and will not precipitate the true manganese ferricyanide but a mixture of the latter and cyanide of iron. Dissolve 3.75 grams of the potassium ferricyanide in water and dilute to 1 liter. 1 c.c. of this solution will precipitate about 0.001075 gram of manganese. See page 200 for the equation explaining the manner in which the manganese is precipitated from an ammoniacal solution by potassium ferricyanide. Add a slight excess of the precipitant and allow the solution to stand a half hour before filtering. Mix some paper pulp with the precipitate, filter it, and wash it with a solution of 5 grams of ammonium nitrate dissolved in 500 c.c. of water made ammoniacal with 5 c.c. of strong ammonia. In order to secure a rapidly subsiding precipitate it is best to make the manganese solution, at first, just ammoniacal enough to turn a small piece of red litmus paper floating in it blue; then add 5 c.c. of 1 : 1 ammonia

water in excess. After washing the manganese ferricyanide as described until 1 c.c. of the washings acidulated with nitric acid no longer give a chlorine test with silver nitrate, it is burned at a low red heat until free of carbon of the filter paper; it then consists of a mixture of oxides of manganese and iron which can be analyzed for manganese as usual. This mixture of oxides of manganese and iron seems to be of fairly constant percentage of manganese if always burned off at definite temperature. The author is not yet prepared to recommend weighing the mixture of oxides as a gravimetric method for manganese. He made many experiments with this in view and obtained some promising results. Where large amounts of manganese are precipitated in this way in the presence of lime, it is advisable to dissolve the mixture of oxides in 20 c.c. of conc. HCl and make a basic acetate separation of the iron; the manganese in the filtrate and washings from the iron acetate is again precipitated as before with ferricyanide and the filtrate and washings from the manganese are combined with the filtrate and washings from the original ferricyanide precipitation of the manganese. In this way the possibility of any lime being carried out with the manganese ferricyanide is obviated. This second precipitate of manganese ferricyanide is burned off with the iron from which it has just been separated, otherwise two basic acetate separations would have to be made at this point instead of one. The total ash contains all of the manganese freed from the lime and magnesia. The manganese can now be determined as on page 188 or under "Second Portion," page 192.

*Lime and Magnesia.* The combined filtrates from the two manganese ferricyanide precipitations are treated with 100 c.c. of conc. nitric acid and evaporated to dryness. This acid should be added to the solution before the evaporation begins, to prevent, as far as possible, the formation of the blue cyanides. When the evaporating solution reaches a certain degree of concentration it should be watched as spraying may begin, and at this stage the casserole should be covered until this action

is over; the cover is then removed and the evaporation continued to dryness. The residue in the casserole is taken up with 100 c.c. of HCl and concentrated to 20 c.c. after the action between the acid and the salts is over. Add 100 c.c. of water; and precipitate the iron with ammonia; filter; wash with water until the washings are free of chloride test obtaining filtrate (A). Redissolve the iron hydrate; and precipitate it again; filter; wash; and combine the filtrate and washings with (A). The combined filtrates and washings are made faintly ammoniacal and the calcium is precipitated with ammonium oxalate as in the analysis of limestone. The oxalate is filtered, washed, and reprecipitated. The two filtrates from the oxalate are combined and the magnesium is precipitated as given on page 334.

*Phosphorus.* Weigh 0.500 gram of the slag into a porcelain dish and with it an equal amount of potassium chlorate; moisten to a thin paste with water and then pour in 50 c.c. of conc. HCl. Heat until all is in solution except the silicic acid, remove the cover and evaporate to dryness but not at a baking heat. Redissolve with 30 c.c. of conc. HCl; and add 50 c.c. of water; filter; wash; convert to nitrates by evaporating twice to 20 c.c. with 50 c.c. of conc. nitric acid; boil with a slight excess of  $\text{KMnO}_4$  and finish as for phosphorus in steel.

#### THE ANALYSIS FOUND.

	Per cent.		
$\text{SiO}_2$ .....	19.45	$\text{MgO}$ .....	5.80
$\text{FeO}$ .....	6.75	$\text{MnO}$ .....	9.00
$\text{Al}_2\text{O}_3$ .....	1.05	$\text{TiO}_2$ .....	5.63
$\text{CaO}$ .....	47.66	$\text{P}_2\text{O}_5$ .....	4.39

## CHAPTER IV.

### PART I.

#### ANALYSIS OF TUNGSTEN POWDER.

FUSE 0.6 gram of the powder with a mixture of 10 grams of carbonate of soda well ground in a mortar with 2 grams of potassium nitrate. A complete fusion is obtained in twenty minutes. The melt is dissolved with water in a platinum dish. It is transferred to a 300 c.c. casserole and acidulated with hydrochloric acid — keeping the dish covered during acidulation. The solution is heated for a half hour with cover on, or until all danger of loss by spraying is over. The cover is removed and the acidulated fusion is evaporated to dryness. 10 c.c. of 1 : 1 hydrochloric acid are then added and the contents warmed until iron is dissolved. 200 c.c. of water are next put into the dish, and the solution is heated for thirty minutes to dissolve all sodium salts.

The precipitated tungstic acid is filtered out and washed free from iron test with very dilute hydrochloric acid. It is washed twenty more times to insure removal of salts. The filtrate and washings are again evaporated to dryness, dissolved, filtered, and washed as before. The second filtrate and washings are treated with a hydrochloric acid solution of cinchonine to remove the last traces of tungstic acid. (See page 109.)

The three portions of the tungsten are burned off at a low red heat until bright yellow. This yellow residue is weighed and fused with 10 grams of potassium bisulphate until the fusion is clear and transparent.\* The melt is cooled and dissolved in a platinum or porcelain dish in a water solution of 15 grams of ammonium carbonate, warming gently to hasten

\* Read page 58.

solution. Remove the dish from the heater as soon as the fusion is dissolved.

The small residue of iron and silica is filtered out and washed free of sulphate test with ammonium carbonate solution. This residue is ignited and weighed, and its weight deducted from the weight of the yellow oxide. The remainder is multiplied by 79.31, and divided by the weight of sample taken for analysis to obtain the percentage of tungsten. If the silica residue is large or has yellowish tints, fuse it again. It may contain tungsten. Unless it is fused again, dissolved in ammonium carbonate and washed and weighed, the tungsten result will be too low. This last weight will be the correct deduction for silica, iron oxide, etc. If the first fusion and preceding operations have been conducted as given, the silica will be practically pure white, containing only traces of other oxides.

When the first bisulphate fusion is being dissolved in ammonium carbonate water, as stated, it should be only warmed to start the action, and the heat should be shut off the moment the bisulphate is in solution, otherwise tungsten may be found with the silica.

*Rapid Method for Tungsten.* Weigh 1 gram of metal into a platinum dish. Add 10 c.c. of pure hydrofluoric acid. Cover with a lid. Warm in a good draught. Remove from fire. Add three or four drops of conc. nitric acid. Violent action occurs at this point. Continue to add nitric acid a drop at a time until further additions of acid produce no action. This will take, in all, about 5 c.c. of conc. nitric acid. Remove the lid, rinsing off its surface, permitting the washings to flow into it. Add 10 c.c. conc. sulphuric acid. Evaporate to thick fumes of SO<sub>3</sub>. Cool, moisten with 10 c.c. of conc. hydrochloric acid. Add 10 c.c. of water, transfer the contents of the dish to a 600 c.c. casserole, and heat to boiling with constant stirring to prevent bumping. Cool. Filter. Wash with 1 : 10

\* Add cinchonine to the filtrate and washings and, after several hours, filter off any tungstate that may have formed, and add it to the main tungstic acid before it is fused with KHSO<sub>4</sub>.

hydrochloric acid until free of iron test.\* Ignite and weigh the tungstic acid as trioxide. Fuse the latter with potassium bisulphate and finish as in the first method. This rapid scheme is a modification of Arnold and Ibbotson's method, and usually gives results one- or two-tenths of one per cent lower than the longer method, which must be resorted to for complete analysis of the powders. (See Arnold and Ibbotson's Steel Works Analysis, 1907.)

*Iron, Phosphorus and Sulphur.*\* If these elements are asked for, 1 gram of sample should be fused with 20 grams of sodium carbonate and 4 grams of potassium nitrate. Then proceed exactly as for tungsten until just before adding the cinchonine. (A) Divide the filtrate and washings, instead of adding the cinchonine, into two equal parts. To one portion add the cinchonine; the small precipitate is burned off and weighed by itself. Evaporate it with a little hydrofluoric and sulphuric acids. Ignite it and multiply its weight by two. Add this amount to the tungsten trioxide found by the two evaporation to dryness. Calculate this total trioxide to percentage on the basis of 1 gram taken for analysis. (B) To the other portion of the divided filtrate and washings obtained after the second evaporation add a slight excess of ammonia. Heat, filter, and wash with hot water. Ignite this precipitate, but do not weigh it, as it is almost sure to contain nearly all of the tungsten that remained in this portion of the divided filtrates. Dissolve it with hydrochloric acid; evaporate off excess of acid; dilute with water; filter out any tungstic acid that may separate, washing the latter free from iron with 1 : 20 hydrochloric acid. The filtrate and washings are evaporated to thick fumes with 60 c.c. 1 : 3 sulphuric acid and reduced with zinc and titrated with the same permanganate standard that is used for iron oxide determinations in graphite (see page 338). Calculate the iron found as metal, and multiply the result by two to obtain the percentage on the basis of 1 gram.

*Phosphorus.* The author has found that the practice of decomposing tungsten-containing materials by fusing them

\* Read page 73.

with a mixture of sodium carbonate and potassium nitrate, leaching out the fusion, acidulating with hydrochloric acid, removing the tungstic acid by several evaporation to dryness, and then using the filtrate and washings from the tungstic acid for the determination of the phosphorus, gives far less than the actual per cent.

The method that he now uses together with the proof of the accuracy of the same, he first published in the *Journal of Ind. and Eng. Chem.*, Vol. 5, No. 4. The full description of his method can be found on page 82.

*Sulphur.* The first filtrate and washings obtained from the ammonia precipitation of the iron are made slightly acid with hydrochloric acid. Barium chloride is added, and the sulphur is finished as in gravimetric sulphur in steels. Multiply the result by 2 to bring it to 1 gram taken for analysis. (Read page 73.)

When sulphur is determined, a blank should be run, beginning with the melting of the same flux. The BaSO<sub>4</sub> obtained is deducted before calculating the per cent of sulphur.

*Carbon.* Burn 3 grams with 4 grams of red lead, deducting the blank due to the lead.

*Manganese.* Fuse 0.100 gram with 2 grams sodium carbonate and 0.5 gram of niter. Remove tungsten by one evaporation to dryness. Dissolve in 5 c.c. 1 : 1 hydrochloric acid; filter; wash; evaporate to fumes with 10 c.c. 1 : 3 sulphuric acid. Dissolve in 10 c.c. of water; wash into a 10 by 1 inch tube; dilute to 20 c.c. with water. Add 10 c.c. concentrated nitric and finish as in steels. Accurate to 2 per cent if 0.050 gram are taken for analysis when the manganese exceeds 1 per cent.

For higher per cents of manganese fuse 1 gram and remove tungsten by one evaporation. Convert the filtrate into sulphate; rinse it into a liter flask and proceed as given for high manganese in ferro-titanium.\*

*Molybdenum in Tungsten Powders.* Fuse 1 gram as for tungsten. Dissolve the melt in as little water as possible. Filter. Wash with sodium carbonate water. Add to the filtrate and washings 4 grams of tartaric acid. Then make

\* Or finish by the author's method given on page 278.

the filtrate very slightly acid with hydrochloric acid. Warm. Pass  $H_2S$  for an hour, or until the brown sulphide settles well. Filter off the sulphide. Wash it thoroughly with  $H_2S$  water. Ignite the precipitate at a very low heat until white or bluish white. If it looks yellow, fuse it with a little sodium carbonate; dissolve the melt in water; add a crystal of tartaric acid and proceed as before with  $H_2S$ .

When the bluish white molybdenum trioxide is obtained, multiply its weight by 0.6666 after deducting the silica, etc. (See Molybdenum in Steel.) The methods given for tungsten powder apply also to ferro-tungsten.

*Silica and Iron.* Instead of removing the silica and iron in the analysis of tungsten powder, as given on pages 68 and 69, by a fusion with potassium bisulphate, the crude  $WO_3$  can be fused with twenty times its weight of sodium carbonate after the silica has been volatilized by evaporation with 15 c.c. of hydrofluoric acid and five drops of conc. sulphuric acid, in the same manner as described for the determination of the silica on page 99. It is to be noted that metallic silicon does not exist as such in tungsten powders but as oxide. Having removed the silica and determined it as given on page 99, and the above fusion with sodium carbonate having been made, the melt is dissolved out in water, and the iron oxide is filtered off; washed thoroughly with water; ignited; weighed; and deducted from the  $WO_3$  plus  $Fe_2O_3$ . The  $Fe_2O_3$  so obtained may contain some alumina and if the actual iron content is desired, the supposed oxide of iron must be dissolved in a few c.c. of conc. HCl and the actual iron determined as given on page 70.

It has been pointed out that sodium carbonate may contain enough iron to make an appreciable error in the tungsten determination by reason of deducting from the crude  $WO_3$  not only the iron that existed in the same but also that which contaminated the sodium carbonate used in the fusion. The remedy is to subtract the amount of iron and alumina in the carbonate from the total iron and alumina found, before de-

ducting the latter from the crude  $\text{WO}_3$ . Credit is due to Mr. Geo. M. Berry for emphasizing this point which is one phase of the general necessity of running blanks on all reagents that one uses for any analysis whatsoever.

*Carbon.* The carbon in tungsten powders can be determined by burning the latter in the electrically heated furnace without any aid to the combustion other than the oxygen. The heating in the stream of oxygen should be continued for 45 minutes. Ferro-tungsten should be as finely powdered as possible. It is mixed with four times its weight of red lead or peroxide of lead to insure complete combustion and the burning should be continued for 30 minutes at least. Blanks must be determined on the oxide of lead used, and deducted from the total  $\text{CO}_2$  found. (See Chapter XI, page 213.)

*Sulphur.* Sulphur can be very accurately determined by fusing in an iron crucible 1 gram of the tungsten powder or the ferro-tungsten with 15 grams of sodium peroxide mixed with 7 grams of sodium carbonate.

The melt is dissolved out in water, in a casserole, and evaporated to dryness after adding an excess of HCl. Proceed from this point to remove the tungsten, as given on page 68, until the last traces of it have been precipitated with cinchonine. The filtrate from the cinchonine tungstate is then precipitated with barium chloride and the sulphur finished as given for steels, page 274. Run complete blanks including every operation. If the cinchonine contains excessive amounts of sulphates, as is sometimes the case, these can be removed by washing the crystals on a porcelain colander with distilled water until the washings no longer give a precipitation with barium chloride solution. This may cause some loss of the cinchonine. A sulphur determination of any tungsten compound should, without fail, have this cinchonine treatment to remove last traces of the metatungstate, otherwise the latter tungstate will contaminate the barium sulphate, frequently causing serious error.

THE DETERMINATION OF OXYGEN IN METALLIC TUNGSTEN  
POWDER AND SOME NOTES ON THE DETERMINA-  
TION OF OXYGEN IN STEEL.

BY CHARLES MORRIS JOHNSON.

*Received January 22, 1913.*

It has been found a distinct advantage both in the manufacture and use of tungsten powders to know their oxygen content. In one of the laboratories under the author's direction, this determination is a matter of daily routine. The method involves the same principle used in the determination of oxygen in steel; i.e., the ignition of the substance in a stream of hydrogen, which method is credited to Ledebur.

The electrically heated furnace introduced by the author \* in 1908 for the direct determination of carbon in iron, steel and alloys is utilized in the process which is described in detail in this paper.

Walker and Patrick,† in a paper read at the Eighth International Congress of Applied Chemistry, attack the accuracy of the Ledebur method on the ground that any oxides of manganese or silicon present in the steel would not be reduced. The author regards the Ledebur method as more practical than the proposed new one† above noted; even if the former process does not reveal the total oxygen present it certainly shows enough of it to furnish a basis for judgment of the quality of the steel. If the steel is sufficiently dirty and poorly melted in actual open-hearth Bessemer or crucible practice to contain oxides of manganese and silicon, then it would surely contain enough oxide of iron to condemn it.

The arrangement of apparatus is indicated in the drawing and the accompanying notes. The towers (or jars), page 77, are the author's design as are also *J*, *I* and *C*, and were first used as part of a combustion train.‡ In this laboratory four furnaces are placed side by side. By the use of a Y tube at the outlet of

\* *J. Am. Chem. Soc.*, 30, 773.

† *Proc. 8th Intern. Cong. Appl. Chem.*, 21, 139; also this Journal, 4, 799.

‡ *J. Am. Chem. Soc.*, 28, 862.

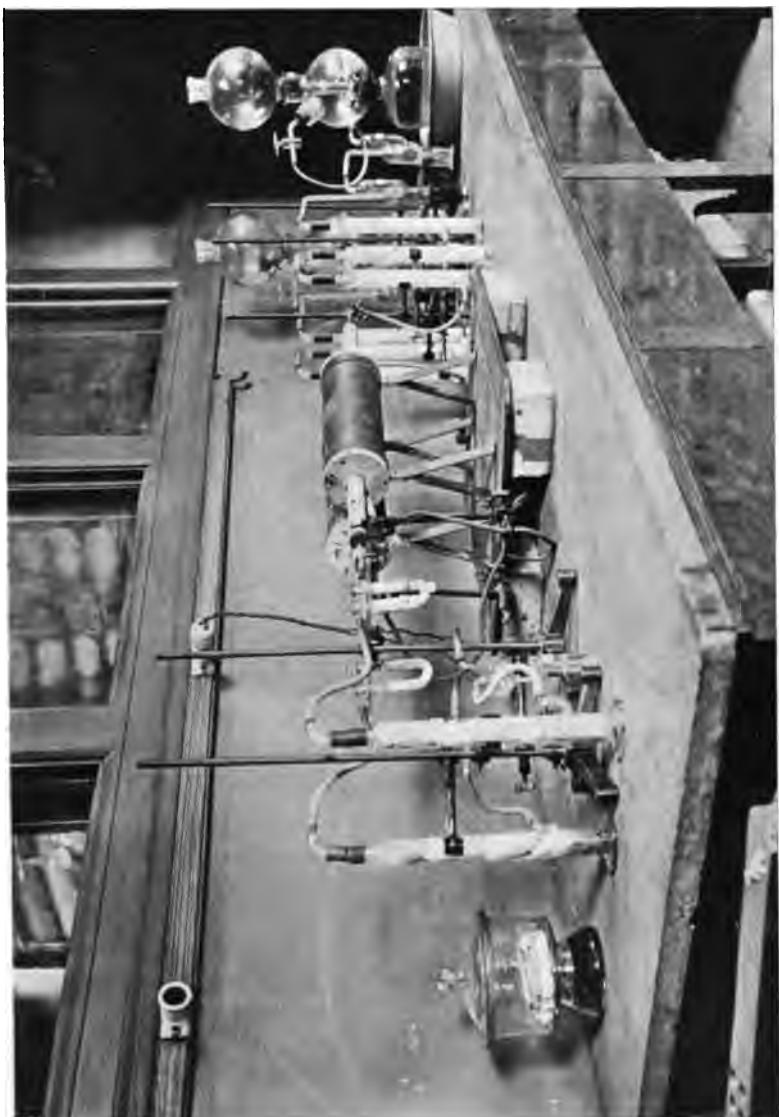


Photo No. 1

jar *F*, one train from *F* to *K* can be made to serve two furnaces.\* Of course a separate set of *A*, *B* and *C* is necessary for each furnace. If, after making a large number of determinations, the blank begins to show a gradual increase, the contents of the various jars must be renewed.

#### METHOD.

*Blank.* Before introducing anything into the electric furnace, close all points marked "screw pinch cock." At *B*, Fig. 1, make a connection with a straight glass tube instead of the U tube shown. Insert quickly into the quartz tube (at the point marked *E*) the porcelain boat that has been kept at 105° C. in an air bath. Push the boat into the center of the furnace with a heavy copper wire which is marked to show how to place the boat in the hottest part of the furnace. Stopper the tube as quickly and tightly as possible. Open all 4 pinch cocks and turn on the hydrogen slowly until it passes through the apparatus at the rate of about seventy bubbles per minute. Allow the hydrogen to pass through the cold furnace for 30 minutes. Close all the pinch cocks and replace the glass tube at *B* by the U tube. Open all cocks and let hydrogen run for another half hour to fill the weighing apparatus with this gas. Close all pinch cocks and the glass cocks on the U tube. Remove the U tube and weigh it quickly. Insert the U tube again, open all cocks and start the hydrogen flow; turn on the electric current in the furnace and bring up the temperature to 950 to 1000° C. After reaching this temperature keep the heat on for two hours with the hydrogen passing continually. Close all pinch cocks, shut off the hydrogen, and close the glass cocks on the weighing apparatus *B*. Detach and weigh *B*. The difference between this weight and the first weight represents the blank to be deducted from all determinations.

*Sample.* Dry the finely ground powder of the tungsten metal to constant weight at 105° C. Put 2 or 3 grams of the powder into a porcelain boat that has been dried at 105° C.

\* See photo No. 1.

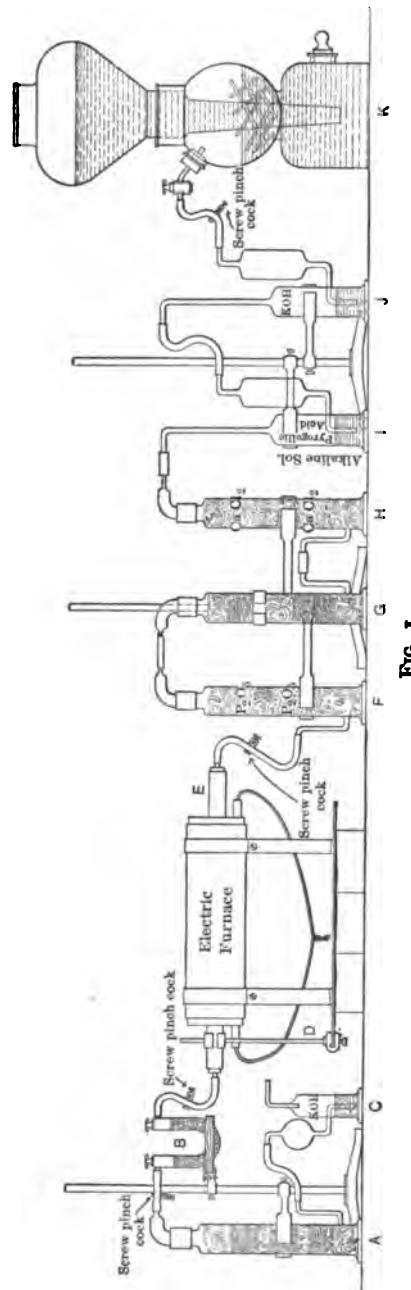


FIG. 1

Place this in the cold furnace and stopper tightly at *E*. Using the glass tube connection at *B*, open the pinch cocks and allow hydrogen to pass through the cold furnace for one-half hour to remove whatever air entered when the charge was inserted. Close all pinch cocks and replace the glass tube by the weighed U tube at *B*. Open all cocks, adjust the hydrogen flow to 70 bubbles per minute and turn on the electric current, heating the furnace to from 950 to 1000° C. Maintain this temperature for two hours with the hydrogen passing. Close all cocks and turn off the hydrogen. Remove and weigh the U tube. The increase in weight minus the blank gives the amount of water formed by the reduction of the metallic oxides to metal. This result multiplied by 16 and divided by 18.016 is equivalent to the weight of oxygen which is converted into percentage by the usual calculations.

#### STANDARDIZATION OF APPARATUS.

*With C.P. Tungstic Oxide.* This material is prepared as follows: Treat 5 grams of 96 to 98 per cent tungsten powder in a platinum dish with 10 c.c. c.p. hydrofluoric acid. Pour on this mixture very slowly 30 c.c. of concentrated nitric acid. This produces considerable heat, and the material is dissolved as clear as water. Now add 15 c.c. of concentrated sulphuric acid, evaporate to thick fumes, cool, add from 10 to 20 c.c. c.p. hydrochloric acid, boil from 3 to 4 minutes, add 50 c.c. of water, heat, filter, and wash free from iron and sulphates by decantation in a 600 c.c. beaker. Transfer to a platinum dish, ignite at a bright red heat in a muffle, and put in a glass-stoppered bottle. Before using any of this material for a test, ignite a portion of it at a blast lamp temperature. Immediately after the blasting put 1 gram of the oxide in a porcelain boat dried at 105° C., and charge it at once into the furnace. It will require at least 6 hours treatment at 950 to 1000° C. to reduce this amount of oxide and carry all of the water formed over into the weighing apparatus.

*With Ferric Oxide.* Dissolve 10 grams of low carbon steel of very low phosphorus, sulphur and silicon content in 100 c.c.

hydrochloric acid in a liter beaker. Transfer this to a No. 7 porcelain dish and evaporate to 10 c.c. Add 100 c.c. nitric acid and evaporate to 20 c.c. Add 50 c.c. of concentrated nitric acid, and evaporate to dryness. Place the dish in a muffle and heat to redness. Cool, dissolve in 50 c.c. hydrochloric acid, add 50 c.c. of water, evaporate to small volume, filter out insoluble matter, such as silicic acid, and precipitate with filtered ammonia. Wash the precipitate by decantation until free from chlorides, dry in a porcelain dish, heat to redness and place in a stoppered bottle. Blast a portion of this for three or four minutes, transfer 1 gram quickly to a porcelain boat, and place at once in the reduction furnace. Pass hydrogen for six hours after the furnace reaches 950 to 1000° C.

TABLE I. RESULTS OBTAINED BY APPARATUS DESCRIBED.

Pure  $\text{WO}_3$ , gave 20.69 per cent oxygen.

1 gram gave 20.70 per cent oxygen.

0.250 gram gave 20.80 per cent oxygen.

0.500 gram gave 20.30 per cent oxygen.

Average, 20.60 per cent plus.

Pure  $\text{Fe}_2\text{O}_3$ , gave 30.05 per cent oxygen.

0.500 gram gave 30.16 per cent oxygen.

Blanks, 0.0030 and 0.0036.

#### THE EFFECT OF FREE CARBON ON THE METHOD.

It is an advantage to have some excess of free carbon in finished tungsten powder, and, at times, in the process of manufacture, it is necessary to know the amount of oxygen present in a powder that contains as much as 3 or 4 per cent of charcoal. Some tests were made to see if the reaction  $\text{WO}_3 + 3 \text{C} = \text{W} + 3 \text{CO}$  might not occur at the same time with the desired reaction  $\text{WO}_3 + 6 \text{H} = \text{W} + 3 \text{H}_2\text{O}$ . Table 2 shows that the presence of excessive amounts of free carbon caused no material error in the case of the pure tungsten oxide, but did cause low results when the carbon content exceeded 5 per cent in the iron oxide. A curious feature is that 30 per cent of free carbon caused practically no lower result than the addition of 10 per cent.

TABLE 2. RESULTS OBTAINED WITH MIXTURES OF OXIDES AND CHARCOAL.

Grams of Mixture.		Percentage Oxygen, Theoretical.	Percentage Oxygen Found.	Percentage Carbon Present.
WO <sub>3</sub>	Charcoal.			
0.544	0.201	20.69	20.57	26.6
0.300	0.090	20.69	19.80	23.0
0.400	0.080	20.69	20.32	16.7
0.500	0.060	20.69	20.53	10.7
Fe <sub>2</sub> O <sub>3</sub>				
0.5785	0.000	30.05	29.84	None
0.473	0.208	30.05	27.35	30.5
0.400	0.122	30.05	28.68	23.3
0.300	0.089	30.05	27.53	23.0
0.500	0.025	30.05	29.95	4.7
0.500	0.050	30.05	27.82	9.7

The following table shows the amounts of oxygen found in the various brands of tungsten powders made both in the U. S. and abroad. Each numeral represents a different make.

The reduction was particularly poor in the second lot received from the German manufacturer designated as II (No. 2 in his second shipment). When so much oxide is present it can be easily detected by the eye, being equivalent to 10.92 per cent of tungstic oxide. Such so-called metal has a distinct brown color.

TABLE 3.

Make.	Imported or Domestic.	Oxygen Found.	Consignment.
		Per cent.	
I.....	German.....	1.02	.....
II.....	German.....	1.10	No. 1
II.....	German.....	2.26	No. 2
III.....	German.....	0.18	.....
IV.....	German.....	0.53	.....
V.....	American.....	0.37	No. 1
V.....	American.....	0.47	No. 2
V.....	American.....	1.24	No. 3
VI.....	American.....	0.80	.....
VII.....	American.....	0.45	.....
VII.....	American.....	0.08	.....
VII.....	American.....	0.07	.....

**THE DECARBONIZATION OF STEEL WHEN IGNITED IN A  
STREAM OF HYDROGEN FOR THE OXYGEN TEST.**

In 1909 the writer called attention to the fact that hydrogen will produce a bark, or decarbonized surface, on steels when the latter are heated in a current of this gas. Supplementing this statement \* the following tests were made on three steels that were analyzed for oxygen:

TABLE 4.

	Grams of Drillings Taken for the Oxygen Test.	No. of Hours Ignited in Hydrogen.	Percentage Carbon Content.	
			Before Ignition.	After Ignition.
Sample I.....	9.6	3 $\frac{1}{2}$	1.04	0.90
Sample II.....	16.0	3 $\frac{1}{2}$	1.08	0.83
Sample III.....	19.5	3 $\frac{1}{2}$	0.83	0.70

In the foregoing method no preheating furnace or tube is used such as was recommended by Ledebur in his "Leitfaden für Eisenhütten-Laboratorien" and adopted by others who have since written on this or similar subjects, thus simplifying matters to that extent. Also, concentrated sulphuric acid is omitted, entirely, eliminating the possibility of unpleasant, not to say dangerous, accidents from this source.

The introduction of an alkaline solution of pyrogallol into the purifying train was made at the suggestion of Mr. Simon Lubowsky, in July, 1912, when working under the author's direction. The latter adopted his suggestion as did Mr. McMillen,† of The Crescent Steel Works, who was the first to apply the electrically heated furnace, introduced by the writer, to the determination of oxygen.

\* See "The Formation of White Scale on Steel and the Surface Decarbonization of Pipe-annealed Steel," page 348.

† Met. and Chem. Eng., 11, No. 2; also this Journal, Feb., 1913.

THE PREPARATION OF THE STEEL SAMPLE FOR THE  
DETERMINATION OF OXYGEN.

The steel should be first thoroughly ground and polished free of all rust and scale as a very small particle of either oxide would seriously impair the accuracy of the work. The drill should be also free of rust, grease and scale. The drilling should be proceeded with slowly so as not to overheat the sample as this will cause oxidation. Any blue or gold colored drillings present indicate overheating during the drilling or milling of the samples and any such should be rejected. 10 coarse drillings are also rejected by the author; and only those drillings that will pass a twenty mesh screen and will not pass a thirty mesh one are used, unless the drillings are very thin. 10 to 20 grams of sample are taken and the work is carried out as in the tungsten powder. The drillings are kept over anhydrous calcium chloride until used. The great danger about the whole operation is that improper sampling may cause oxygen to be found that does not exist in the steel. The drillings are heated at 950 to 1000° C. for 2 hours in the apparatus shown on page 77, Fig. 1.

THE DETERMINATION OF PHOSPHORUS IN FERRO-TUNGSTEN  
METALLIC TUNGSTEN POWDER, TUNGSTEN OXIDE  
AND TUNGSTIC ACID BY DIRECT SOLUTION.

BY C. M. JOHNSON.

*Received February 7, 1913.*

The author found in the course of an investigation that the practice of decomposing tungsten-bearing materials by fusing them with a mixture of sodium carbonate and potassium nitrate, leaching out the fusion, acidulating with hydrochloric acid, removing the tungstic acid by several evaporation to dryness, and then using the filtrate and washings from the tungstic acid for the determination of the phosphorus, gave far less of the latter element than was actually present. He then devised the following method which he has found to give near enough to the true phosphorus for technical purposes.

## FERRO-TUNGSTEN.

Add 30 c.c. of concentrated nitric acid to 1 gram of the powdered sample, in a platinum dish; then add slowly 3 c.c. of c.p. hydrofluoric acid. Keep the dish covered with a watch glass; warm the mixture. After warming and slight boiling, the material should dissolve to a clear solution. Transfer the solution to a No. 5 porcelain dish and evaporate to dryness; do not bake as there is danger of losing phosphorus at this point. Dissolve this residue with 50 c.c. of concentrated hydrochloric acid. Heat with the lid on; then remove the lid and evaporate to dryness; do not bake. Dissolve again, using 20 c.c. of concentrated hydrochloric acid; heat; add 50 c.c. of water, stir, heat and filter out the main tungsten; wash with one part of concentrated hydrochloric acid diluted with twenty parts of water. Evaporate the filtrate and washings to 10 c.c., add 20 c.c. of water, stir and filter as before. Evaporate to 10 c.c., add 75 c.c. of concentrated nitric acid and heat with the cover on until all action is over; remove the lid and evaporate to 20 c.c. Add 50 c.c. of nitric acid, and evaporate to 15 c.c. Add 20 c.c. of water, stir, heat and filter into a 6 oz. beaker; wash with 2 c.c. of concentrated nitric acid diluted with 100 c.c. of water, washing fifteen times. Evaporate the filtrate and washings in the beaker to 40 c.c. Replace the lid and add a slight excess of 5 per cent solution of potassium permanganate; boil three or four minutes. Dissolve the excess of manganese oxide with a little ferrous sulphate, and precipitate the phosphorus with molybdate solution.

When dissolving ferro-tungsten in the mixture of nitric and hydrofluoric acids, a porcelain dish can be used, but a little more hydrofluoric acid may be needed to secure complete solution of the alloy on account of the tendency of the latter acid to attack the dish. Further, when a porcelain dish is used, blanks must be run, using a standard steel. The latter is dissolved in the *mixture* of the two acids and the phosphorus determined, using the porcelain dish. If the standard is found to

run higher than it should, the deduction necessary to correct it constitutes the blank to be subtracted from the phosphorus found in the sample.

Any method with which the writer is acquainted, using a carbonate and niter fusion of materials containing tungsten for the purpose of obtaining the percentage of phosphorus therein, gives only a fourth, or less, of the actual content of the latter element. The following results are only a few of those obtained in this laboratory and are given in proof of the above statement.

#### COMPARISON OF FUSION AND EXTRACTION METHODS.

Sample.	Percentage, Author's Extraction Method.	Phosphorus Found by Fusion with $\text{Na}_2\text{CO}_3 + \text{KNO}_3$
Ferro-tungsten No. 18.....	{ 0.322 0.350 0.345 0.330}	{ 0.096 0.088}
A high phosphorus pig iron (0.73 per cent P): 0.5 gram tungsten powder (98 per cent pure) per gram of iron.....	0.70	{ 0.098 0.095}
"Tungsten cake".....	{ 0.101 0.102}	{ 0.008}
Tungsten powder oxidized to $\text{WO}_3$ at low red heat before extraction.....	0.113	0.007

#### TUNGSTEN ORES.

Here the procedure differs only in the manner by which decomposition is effected. Grind the ore to the finest possible state of division; extract at nearly boiling temperature with 100 c.c. conc. hydrochloric acid in a No. 5 porcelain dish. About every thirty minutes, add 0.1 gram additions of  $\text{KClO}_3$ ; on each addition of chlorate stir the sample off the bottom of the dish with a glass rod. Continue the heating, addition of chlorate and stirring until the tungsten ore has changed from a brown color to yellow in case of the dark ores; or from a light gray or brown to a very bright yellow in case of

scheelite ore. Evaporate to dryness; cover; add 50 c.c. concentrated HCl; heat 10 minutes to dissolve the iron and manganese; add 50 c.c. of water and heat 15 minutes to allow the tungstic acid to separate well; cool and mix in some paper pulp. Filter through a double filter; wash with one part of hydrochloric acid diluted with twenty parts of water. Evaporate the filtrate and washings to 5 c.c. and add 75 c.c. of concentrated  $\text{HNO}_3$ ; heat with the cover on the dish until all red fumes are gone and no further spraying occurs; remove the cover again and evaporate to 10 c.c.; add 50 c.c. of concentrated nitric and evaporate to 10 c.c. again; dilute with 15 c.c. of water and mix well. Filter into a 6 oz. beaker; wash with a 1 per cent by volume solution of nitric acid, fifteen or twenty times. Evaporate the filtrate and washings to 40 c.c. in the beaker; boil with a slight excess of permanganate solution. Add just enough ferrous sulphate to clear the excess of the hydrated oxide of manganese and boil again five minutes. Add 50 c.c. of molybdate solution to the hot fluid in the beaker and finish the analysis as given for ferro-tungsten.

By careful heating and small additions of the chlorate, together with further applications of acid, if necessary, many dark ores can be so completely decomposed as to attain a clean orange color. The more complete the decomposition, the more perfect will be the extraction of the phosphorus. The hard black ferberites are the slowest to yield and take on the yellow color. The decomposition can be done to the best advantage at a low digesting heat and will require at least 5 or 6 hours.

This somewhat lengthy method is the only one that the author has found reliable, thus far, for technical purposes in tungsten ores. The latter may contain all the way from slight traces up to 0.500 per cent phosphorus. The fusion method with these ores gives just as low results as with the ferro-tungsten. The cause of the low results is the formation of phospho-tungstic acid; this is carried from the solution with the main tungstic acid that forms when the sodium tungstate is decomposed by acidulation and evaporation with acid.

### METALLIC TUNGSTEN POWDER, TUNGSTIC OXIDE AND TUNGSTIC ACID.

Ignite the tungsten powder at a red heat with frequent stirring until it is all converted to the yellow oxide. Then extract exactly as in tungsten ore for at least six hours and finish according to the ore method.

The original oxidation is best accomplished by weighing the sample into the dish in which the extraction is to be made and then placing dish and all in a muffle which is at a low red heat.

Tungstic acid and oxide do not require heating to redness. Their analysis for phosphorus is exactly like that for ores beginning with the hydrochloric acid chlorate treatment.

Reserve the tungsten residues that are filtered out after the extractions and evaporation for the tungsten determination. The purification of these residues will be made the subject of a later publication.

NOTE.— It may be well in this article to caution those who have occasion to determine the phosphorus in molybdenum compounds, that any molybdic acid separating out of acid solutions containing phosphorus will carry a considerable amount of the latter element out, forming the analogous compound phospho-molybdic acid.

### METHOD.

#### *The Determination of Tin in Metallic Tungsten Powder.*

Weigh 1 gram of finely ground sample into a porcelain boat of size  $2\frac{3}{4}$  inches  $\times \frac{1}{2}$  inch. Spread this material out in as thin a layer as possible. Place this boat in the quartz tube of the same apparatus as is used for the determination of oxygen. Let the hydrogen pass at  $950^{\circ}$  C. or thereabouts for one hour. The hydrogen should pass through the furnace considerably faster than it does for oxygen determination. Turn off the current and continue to pass hydrogen until the furnace is cooled sufficiently, i.e., below a red heat, so that the hydrogen will not explode when the stopper is removed for withdrawal

of the boat. All the contents of the boat should now have the gray color of metallic tungsten. Unless it has this color, it should be returned to the furnace and heated further as before. When the material is properly reduced, remove it to a small agate mortar; pulverize it, taking care not to lose any of the substance. Then transfer the finely ground tungsten powder to a 5 inch casserole; add 100 c.c. of concentrated hydrochloric acid; heat the dish for 6 hours in boiling water, with frequent small additions of potassium chlorate. Add about 1 gram of this salt every hour. Stir the material well off the bottom of the dish with each addition of the potassium chlorate. Add 100 c.c. of water; stir well; filter; wash with dilute hydrochloric acid water; add 10 c.c. of cinchonine solution; dilute to 400 c.c. with water; stir thoroughly; let stand over night; filter from any precipitate of tungsten cinchonate; wash with solution containing 5 c.c. of cinchonine solution, diluted with 500 c.c. of water; add ammonia to the solution of the sample until the iron precipitate, or other precipitates that may have formed, seems to dissolve rather slowly. Heat the perfectly clear solution to about 80° C.; pass H<sub>2</sub>S slowly through it until the precipitate of tin sulphide separates out well. This will take several hours passage of the gas. Filter. Wash with H<sub>2</sub>S water. It will require about 50 to 60 washings to remove the iron. Burn the filter paper and sulphides of tin, copper, molybdenum, etc., at a red heat in an open porcelain crucible until the residue is of a grayish white; if copper is present there will be black spots in the ash. If tinged with red, iron is present. In either case warm the ash in the crucible with 10 c.c. of 1.20 nitric acid, covering the crucible with a small watch glass during the heating period which should continue until any slight effervescence that may occur has ceased. If bismuth be present, it is quite noticeably reduced during the removal of the carbon of the filter paper. After heating for, at least, ten minutes, and longer if necessary, the watch glass is removed, rinsing off its under surface and allowing the washings to run into the crucible. Evaporate the contents of the crucible to dryness and gently

ignite it until all nitrates are decomposed. Then weigh the residue, after igniting it at a red heat for 30 minutes to render the tin insoluble. This weight will be that of the oxides of Sn, Cu, Mo, Sb, Bi and a little Fe. To remove the Cu, Fe and Bi warm the ash in the crucible with 10 c.c. of 1 : 1 HCl, heating for 10 minutes just below boiling; rinse the contents of the crucible onto a small filter; wash the same with 1 : 20 HCl and, finally, with some water. Ignite the paper in the same crucible again until white to grayish white at a low red heat. Moisten with conc. nitric acid and ignite again to oxidize any metal formed.

If molybdenum is present extract this residue with 5 or 10 c.c. of strong ammonia. Use ammonia that is freed from any sediment or floating particles, or scales of glass. Filter; wash paper with ammonia and put it back again into the same crucible, and burn the residue at a low heat. This residue will now consist of tin oxide plus a little silica. Weigh the residue; and remove it to a platinum crucible. Add four to five drops strong sulphuric acid, and then 10 c.c. c.p hydrofluoric acid; evaporate as in the determination of tungsten. Drive off sulphuric acid; weigh the white to grayish white residue as oxide of tin. This weight multiplied by 0.7880 gives the equivalent weight of metallic tin, which is converted to percentage by the usual calculations.

*In the presence of much tin and bismuth* it is more accurate to proceed as given in the foregoing method until the sulphides of tin, etc., have been filtered and washed when, instead of igniting the same, the mixture of sulphides is placed, filter and all, in a porcelain casserole, covered with yellow ammonium sulphide and warmed on a water bath with frequent stirring for three hours. The pulp and solution are then filtered and washed with water containing 10 c.c. of the yellow ammonium sulphide diluted with 500 c.c. of water. After thorough washing the filtrate and washings are made slightly acid with HCl and saturated with H<sub>2</sub>S when all of the tin will separate out; it is then filtered out; washed with H<sub>2</sub>S water; ignited; treated with

nitric acid; ignited again and weighed as tin oxide, now free of bismuth, all of the latter having been filtered out with the paper pulp, as sulphide, after the ammonium sulphide extraction.

If the amount of tin and bismuth in solution is large, for example 100 mgs. of tin and 50 mgs. of bismuth, it is advisable to again heat the precipitated sulphide of tin as before with the yellow ammonium sulphide, when the tin sulphide should be free of bismuth.

The combined filtrates from the two extractions of the tin sulphide are made slightly acid and the bismuth therein is precipitated with  $H_2S$ ; washed with  $H_2S$  water; ignited at a low red heat in a porcelain crucible; the oxide of bismuth is heated with a mixture of a little conc.  $HNO_3$  and conc.  $HCl$  until all black metallic residue is dissolved; it is then evaporated to dryness with an excess of nitric acid; ignited to the yellowish  $Bi_2O_3$ ; and weighed as such and calculated to percentage by use of the factor 0.89655.

For the separation of as much tin and bismuth as mentioned, use 140 c.c. of conc. ammonia saturated with  $H_2S$  for each extraction; and dissolve 1 gram of flowers of sulphur in this amount of ammonium sulphide before pouring the latter over the mixture of the sulphides.

## CHAPTER IV.

### PART II.

#### SAMPLING OF TUNGSTEN ORES.

##### (1) THE JAR MILL.

About two years ago the writer installed in a laboratory under his supervision a jar mill consisting of jars of five pounds capacity. The jars are of the finest grade of German porcelain filled about  $\frac{2}{3}$  full of the highest grade of hand picked, imported flint pebbles. These latter are of an approximately elliptical shape with their shorter axis varying in length from five-eighths to one inch. Each jar is charged with 9.8 pounds of pebbles. The jars are  $8.75 \times 9.65$  inches outside measure. The mill is operated by an electric motor and the jars are run at 60 r.p.m. The jars are filled to the utmost capacity at which the pebbles will do any grinding at all, that is, five pounds, at least, must be charged into each jar. If an appreciably smaller amount is used then the pebbles do begin to abrade on each other and the silica content increases. If much more than five pounds are put in a mill of this size then the reduction of the sample is extremely slow. The sampling procedure is as follows: When the ore is received in lump it is crushed under cast iron wheels to pass an eight mesh screen. About eighty-five per cent of the crushed material is much finer after this reduction, and would pass a thirty mesh. After the material is screened, it is put back in the sacks and a sufficient portion is taken from each bag to provide a forty to fifty pound sample. This is thoroughly mixed and quartered down to about six pounds. Before quartering the fifty pound sample it is spread out in a layer of not above  $\frac{1}{2}$  inch thickness, and is divided into squares of two inches in area. From each square some ore is taken for hand grinding,

leaving at least a remainder of five pounds for the pebble mill. The five pound sample is ground in the jar for from ten to twelve hours. This reduces the ore to the fineness of wheat flour, and secures an absolutely uniform sample. The smaller sample accumulated from the squares is well mixed and is in turn spread into a layer of  $\frac{1}{8}$  inch thickness and sampled again in squares to about ten grams. The latter amount is then ground in an agate mortar.

## RESULTS OBTAINED FROM THE TWO METHODS OF SAMPLING.

	Five Pound Sample Ground in the Jar Mill.		Ten Gram Sample Ground in the Agate Mortar.	
	Per cent $WO_3$	Per cent $SiO_2$	Per cent $WO_3$	Per cent $SiO_2$
Portuguese wolframite.....	70.59	1.87	70.51	1.84
Australian wolframite.....	69.29	5.23	69.30	5.33
Wolframite from the "Straits".....	66.00	2.38	65.96	2.34
Wolframite from the "Straits," Lot A.....	68.81	3.73	68.88	3.62
Portuguese wolframite.....	70.70	2.04	70.79	2.15
"Straits" wolframite.....	70.37	2.04	70.46	2.04
Portuguese wolframite, car 560,151.....	70.34	2.09	70.52	1.85
Wolframite from Randsburg, Cal....	73.58	2.60	73.48	2.64
Straits wolframite, car 10,155.....	69.08	1.95	69.00	1.92
Canadian scheelite.....	71.82	4.20	71.88	4.20
Portuguese wolframite, car 52,974.....	70.48	1.87	70.4	....
	Six Pound Sample Ground in the Jar Mill.		Ten Gram Sample Ground in the Agate Mortar.	
	Per cent $WO_3$	Per cent $SiO_2$	Per cent $WO_3$	Per cent $SiO_2$
S. S. Patricia, car 58,714.....	66.00	5.73	66.00	5.72
California scheelite, car 26,440.....	69.23	7.47	69.10	7.49
Australian wolframite, car 534,453.....	66.6	2.33	69.5	2.40
Wolframite S. S. Cleveland W-1.....	69.6	1.06	69.7	1.05

After making these tests extending over several months the author came to the following conclusions:

- (1) The best grade of porcelain and of hand picked flint pebbles must be used.

(2) The jar must be filled with enough of the sample to prevent the pebbles from rubbing on each other or on the walls of the jar, i.e., a jar calling for a maximum charge of five pounds, for example, must be used with that amount in it, otherwise notable amounts of silica will be gathered up during the grinding. On the other hand practically no silica is obtained and no appreciable lowering of the tungsten content was noted except in one instance car 11,611 was apparently lowered in tungsten content from 72.18 to 71.95.

(3) The proper amount of material to place in a jar of a given size in order to secure perfect grinding, without adding silica, should be determined by experiment.

(4) The great advantages of this apparatus are that a large sample can be taken; that perfect grinding and perfect uniformity of sample are obtained; and that the grinding goes on leaving the operator free to attend to other work.

(5) The only disadvantage is the first cost, but in a large works where many shipments must be sampled, the saving of labor makes the cost insignificant.

(6) The pebble jar mill sample is by far the best for factory control work.

#### Determination of Tungsten in Tungsten Ores.

##### (2) THE DETERMINATION OF TUNGSTEN IN ORES WITHOUT A PRELIMINARY FUSION.

The writer has always refused to assay tungsten ores or other tungsten-bearing materials by precipitation as mercurous tungstate for the reason that any phosphorus, molybdenum, aluminum or vanadium present would be precipitated with the tungsten and counted as such. Tin also is a common constituent of tungsten ores. The writer has often encountered the presence of this element in shipments of wolframite ores from traces up to 3.50 per cent. The sodium carbonate fusion of the ore which is the usual preliminary to the mercurous nitrate precipitation contaminates the sodium tungstate with

tin stannate. In scheelite ores it is a common thing for the phosphorus to be as high as 0.150 per cent and sometimes as much as 0.350 per cent. Slimes and other low grade concentrates are especially liable to be high in this element. The writer has had some residues very rich in tungsten running to 0.400 per cent. Alumina is a frequent constituent to be guarded against. Again, as is well known, it is extremely difficult to wash sodium salts out of tungstates precipitated from a solution of the former by mercurous nitrate.

After some years experience in this line of analytical work, a method was evolved which is perfectly fair both to buyer and seller. It avoids the tedium of the sodium carbonate fusion of the main sample and all of the unpleasantness and inherent inaccuracies of the mercurous precipitation. After more than two years almost daily use of this method the author now gives it in detail feeling confident that those having experience in this line of analytical work will come to see its advantages and will adopt it as giving the true tungsten.

#### METHOD.

The ore is ground to the finest flour either by hand in the agate mortar, or in the laboratory jar mill; after drying this powder for two hours at 105° C., one gram of it is weighed into a 4½ inch casserole of R. B. type with porcelain handle. 100 c.c. of conc. hydrochloric are poured on the ore; the dish is covered with a watch glass and heat is applied for one hour, keeping the acid below boiling. 200 mgs. of crystals of potassium chlorate are now quickly added, covering the casserole again. After the first violent action is over, the ore is carefully and completely stirred off the bottom of the casserole and the mild digesting heat is continued for another hour when the same amount of chlorate is again added and the sample is again stirred up and so on until about 2 grams of the chlorate have been consumed and the ore has been thoroughly decomposed as shown by its color having changed to bright yellow, or in some ores to an orange shade. Scheelite requires 4 hours of this

treatment for decomposition; the dark ores, wolframite and ferberite, turn yellow in 6 hours. The watch glass is then removed and its under side is rinsed off with water, allowing the rinsings to run into the casserole, the contents of which are now evaporated to dryness on a graphite bath, consisting of a six inch pudding pan filled a little over half full with chip graphite. Each unit is heated by an ordinary Bunsen burner and requires but very little gas, a flame from 1 to  $1\frac{1}{2}$  inches in length being sufficient for all kinds of evaporation. The layer of graphite is from  $\frac{3}{4}$  to 1 inch thick. This enameled pan is mounted on a clay flame guard or support. If it is desired to raise the temperature of the dish to a dull red, the pan can be removed and the flame length increased. This combination is acidproof to a practical extent; occasionally it becomes necessary to remove the Bunsen burner and pour a little 1 : 1 hydrochloric acid through the tube to clear it out. After rinsing out the acid with water, it is ready for use again. The graphite is indestructible and the whole outfit is quite inexpensive and lasts a long time. Illustration No. 34 shows twenty-four of these units in use and No. 33 gives a closer view of a portion of a group. The outside depth of the pan is  $1\frac{3}{4}$  inches. (See page 415.)

After evaporating the decomposed ore to dryness 30 c.c. of conc. hydrochloric acid are poured on it; heat is applied; 70 c.c. of water are added, followed by 30 minutes further warming, and some stirring. The crude tungstic acid and silica are filtered through a double, 11 cm. ashless filter. Before performing the filtration, a  $\frac{3}{4}$  inch ball of ashless filter pulp is thoroughly mixed with the tungstic acid to hasten filtration and secure a perfect washing. The mixture on the filter should be washed with great care, giving it not less than sixty washings with 1 : 30 hydrochloric acid to insure removal of potassium salts. If the glass rod or the casserole shows yellow stains of tungstic acid, these can be removed by pouring over them a few drops of conc. ammonia. This solution is then rinsed with a thin jet of water into the filtrate and washings from whence it is recovered along with any metatungstates as fol-

lows: 50 c.c. of cinchonine solution are stirred into the filtrate and washings which are then allowed to stand for from 6 to 12 hours to permit the last traces of the tungsten to separate out. It may be of interest, in passing, to state that when determining sulphur in tungsten-bearing materials of any kind by the barium sulphate method, the writer always first removes the last traces of tungsten that are almost certain to be present by means of 12 hours standing with cinchonine added. It is easily seen that a few milligrams of tungstic acid contaminating the barium sulphate would cause a serious error. Cinchonine used for such work must be first washed free of sulphates before using it. This can be easily done by placing the crystals on a large filter paper and rinsing them with distilled water until the washings no longer give a cloudiness with barium chloride. Any tungsten-cinchonine precipitate must be washed with water containing some cinchonine solution as the precipitate is soluble, or runs through the filter if washed in the same manner as the tungstic acid.

The filter papers carrying the tungstic acid, and that obtained by the cinchonine are dried in an air bath and then smoked off in a 20 c.c. platinum crucible. The heat is then raised to low redness only, and the heating is continued until the residue is yellow and free of carbon. This ash is cooled in a desiccator and weighed as  $\text{WO}_3$  plus some  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{CaO}$  and all of the  $\text{SiO}_2$ . For extreme accuracy in silica the filtrate and washings from the tungstic acid should be evaporated again to dryness before adding the cinchonine; the residue dissolved as before in hydrochloric acid and water; any small residue of  $\text{WO}_3$  plus  $\text{SiO}_2$  so obtained is filtered out; washed; burned with the principal precipitate and then the cinchonine solution is added to get the final traces of dissolved metatungstates.

The weighed residue consisting of total  $\text{WO}_3$  plus  $\text{SiO}_2$  plus the other oxides mentioned is now evaporated with from five to ten drops of conc. sulphuric acid together with 15 c.c. of c.p. hydrofluoric acid in a muffle furnace lined with  $\frac{1}{4}$  inch asbestos.

to board to prevent bits of brick from dropping in the work. The writer uses for these evaporation a small reverberatory furnace. The gas flame is not allowed to come above the bridge wall. By heating in this manner there is never any danger of loss of analyses by spattering. (See page 363.)

The crucible is left in this drying furnace until the heavy white fumes of sulphuric anhydride are no longer given off. The crucible is raised to a dull red heat on a Chaddock burner and then cooled in a desiccator and weighed again. The difference between this weight and the weight of the  $\text{WO}_3$ , etc., should equal the silica present in the ore. But if the per cent so found should exceed 8 per cent  $\text{SiO}_2$ , then it is safer to repeat this evaporation to insure the complete removal of the silica. The author has found that this second evaporation, with additional sulphuric and hydrofluoric acids, should in no case be omitted when the silica content reaches from 30 to 60 per cent as it often does in unconcentrated ores and slimes. Titanic oxide is frequently present with the  $\text{WO}_3$ , etc., and for this reason the sulphuric acid should always be added in at least the quantity specified to prevent its volatilization as fluoride.

After weighing the now silica-free  $\text{WO}_3$ , etc., it is fused at a bright red heat with twenty times its weight of anhydrous sodium carbonate. It is kept molten for twenty minutes. The melt is dissolved in hot water in a 100 c.c. platinum dish, or if no platinum is available, then the fusion can be leached in a porcelain vessel, but in the cold, as otherwise the porcelain will be attacked and the accuracy of the analysis will be impaired.

If the water solution of the sodium carbonate fusion of the silica-free  $\text{WO}_3$  has a greenish tint due to the formation of sodium manganate, a few drops of alcohol are added and the solution is warmed until this color disappears, the manganese completely precipitating as hydrated oxide. A little paper pulp is added; the various oxides are filtered out; washed repeatedly to entirely remove the sodium salts; ignited at a red heat to remove the carbon. If the residue in the crucible sinters on ignition it is imperfectly washed and contains sodium salts, and a repe-

tition of the fusion, solution and washing is necessary. It is safer to fuse the ignited oxides again in any case if their total weight exceeds 4 or 5 mgs., as part of this weight is almost certain to be  $\text{WO}_3$ . After the second fusion, solution, washing, and ignition, the oxides are weighed and their amount is deducted from the weight of  $\text{WO}_3$  obtained after expelling the silica. The remainder represents the total  $\text{WO}_3$  plus any tin and aluminum oxides that may have gone into solution as stannate and aluminate of sodium. To correct for these two elements the filtrates and washings from the two fusions of the oxides of  $\text{WO}_3$ , etc., are made distinctly acid with hydrochloric acid, and then strongly ammoniacal with filtered ammonia. The volume of the filtrates and washings before acidulation and addition of ammonia should be not less than 500 c.c. After adding the excess of ammonia, the solution should be clear, any tungstic acid that may have formed on acidulating having completely dissolved in the excess of ammonia. The solution is now warmed for an hour when any aluminum or tin present will gradually separate out as snow white flakes. These are then filtered out and washed with ammonium nitrate water (5 grams of the nitrate dissolved in 500 c.c. of water), mixing in a little paper pulp, and washing at least fifty times to insure removal of soda salts. The filter is ashed, ignited and weighed, and the weight is deducted from the weight of  $\text{WO}_3$  plus tin and aluminum oxides last referred to. The remainder constitutes the pure  $\text{WO}_3$  in the sample and is then calculated to percentage as usual.

The foregoing method is not interfered with in case niobium and tantalum are present, as the precautions given for the removal of the various oxides mentioned will also eliminate  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$ .

## CHAPTER IV.

### PART III.

#### TUNGSTEN, SULPHUR, SILICON, MANGANESE AND PHOSPHORUS IN TUNGSTEN STEEL AND CHROME TUNGSTEN STEEL.

##### *First Method for Tungsten in Steel.*

If the sample contains considerable chromium and tungsten, proceed as follows: Weigh from  $1\frac{1}{2}$  to 2 grams of drillings (see pages 218-223) into a No. 5 Royal Berlin porcelain evaporating dish. Add slowly to the drillings, keeping the dish covered with a watch glass, a mixture of 30 c.c. conc. hydrochloric acid (1.20 specific gravity) and 30 c.c. conc. nitric acid. Mix the two acids thoroughly before applying them to the steel if phosphorus is wanted. Heat until action ceases, and if the residue in the bottom of the dish is not bright yellow, repeat the addition of acid and continue to heat the dish until the tungsten residue is a clean yellow. Then remove the cover and evaporate the contents of the No. 5 dish to 15 c.c. Keep the heat low enough to prevent spattering. Do the evaporating on a graphite or sand bath. A six inch\* pudding pan filled two-thirds full of graphite heated by an ordinary Bunsen burner makes a simple contrivance for the evaporation. The pan can be set on a tripod or an earthenware flame guard with the burner directly under the center of the pan. With such an arrangement, a flame an inch long will furnish sufficient heat. The guard answers the twofold purpose of supporting the pan and shielding the flame from currents of air. The earthenware has the additional advantage of being acidproof. Add 50 c.c. conc. nitric acid. Put the watch glass on the dish and heat until action ceases.

\* See photo 33, page 415.

Remove the cover and evaporate to 15 c.c. Again add 50 c.c. conc. nitric acid and evaporate to hard dryness. Ignite the dish and its contents to a dull red, raising the heat *slowly* to prevent cracking. Set the dish over a bare flame for this purpose. The terra cotta flame guard, with the pan removed, answers quite well for a support during the ignition. Lower the flame slowly and set the dish on a warm place, cooling it gradually. When the dish is just warm, pour into it 50 c.c. of conc. hydrochloric acid. Put the cover on and heat to slow boiling. Continue to boil until the residue in the bottom of the dish is bright yellow. Then remove lid and evaporate to 51 c.c. Cool, and add 30 c.c. distilled water and ashless paper pulp. Filter on a double 11 cm. ashless filter (a double filter will run faster than a single one); wash with 1 : 20 hydrochloric acid until the washings give no test for iron with potassium or ammonium sulphocyanate. Return the filtrate and washings to the No. 5 dish for concentration.

Roast the paper out of the residue of tungstic and silicic acids in a weighed 20 c.c. platinum crucible. Do not heat tungstic acid to a bright red, as it slowly sublimes at high temperature. When the ash is bright yellow, free from black, cool in a desiccator and weigh. This weight will consist of mainly tungstic acid and silica contaminated with a small quantity of oxides of iron, and chromium, also, if the latter element be present. Add three drops of 1 : 3 sulphuric acid to the residue, and fill the crucible two-thirds full with c.p. hydrofluoric acid. Evaporate in a good draft to moist dryness. Drive off the sulphuric acid by heating the crucible near the top. When all heavy fumes are gone, heat to low red and weigh as  $\text{WO}_3 + \text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ . The difference between this weight and the first weight is the silica which has been volatilized. This loss of weight multiplied by 47.02 and divided by the weight of sample taken, equals the per cent silicon present in the steel. In the meantime the filtrate and washings from the first filtration should be evaporating until a slight ring of basic iron forms around the margin of the fluid. This ring dissolves rather slowly when the dish is rocked backwards and forwards. In

other words, leave only enough acid to keep the iron in solution. (However, care must be taken not to overdo the removal of the excess of acid, as basic iron may separate in the solution when it is heated for the precipitation of phosphorus.) Add 20 c.c. of water; filter through a 9 cm. ashless filter into a 150 c.c. beaker. Wash the residue on the filter until all yellow color due to chloride of iron is gone. About 15 washings should suffice. Wash every other time with 1 : 20 hydrochloric acid. If the volume of the filtrate and washings is over 50 c.c. reduce it to that amount by evaporation. Heat to boiling, remove from fire, precipitate with molybdate solution, and finish the phosphorus as in steels. The residue obtained from the second evaporation of original filtrate from the tungstic acid, etc., after being washed free of color of iron chloride, is further washed free of iron test and burned off in the same platinum crucible with the residue from which the silica was removed by hydrofluoric acid. This total residue which constitutes the tungsten oxide plus small quantities of iron and chromium oxides is weighed again. If the original tungstic acid was thoroughly clean and yellow before the first evaporation to 15 c.c., then the amount of chromium oxide is negligible.

The  $\text{WO}_3 + \text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$  residue is fused with five grams of carbonate of soda. The melt is dissolved with hot water. The small residue of iron is filtered out and washed free of carbonate. It is burned to a red flake in the same crucible, which meanwhile has been thoroughly rinsed free of carbonate with distilled water. The residue is weighed and its weight deducted from the weight of the  $\text{WO}_3 + \text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$ .

If the filtrate from the carbonate fusion is quite yellow, make it acid with sulphuric acid, boil with a slight excess of permanganate, and determine the chromium as in steels.\* Calculate the milligrams of chromium found to chromic oxide, and deduct it from the  $\text{WO}_3 + \text{Cr}_2\text{O}_3$ . The remainder is the tungsten oxide, which multiplied by 79.31 and divided by the weight taken for analysis gives the percentage of tungsten. If the

\* Or determine the chromium by color, page 31.

filtrate from the sodium carbonate fusion is only slightly yellow, the chromium may be ignored in the calculations.

(A) An excellent way to remove oxides of silicon, iron\* and chromium from the tungstic oxide is to fuse with five grams of potassium bisulphate. This fusion can be made quickly. Heat the crucible at first to a very low heat, below redness, until the bisulphate is molten and slight fumes of sulphuric anhydride appear. Then raise the heat carefully to low redness. Keep the lid on the crucible, raising it only slightly to observe the progress of the fusion. When redness has been reached and all danger of spattering is over, raise the lid, and if the contents of the crucible are in a state of transparent fusion, with no yellow specks left undissolved, the fusion is completed. One can see the bottom of the crucible through the transparent molten mass, and, if only pure white flakes of silicic acid are floating about, the melt is perfect. Cool. Dissolve in 10 grams of ammonium carbonate and 100 c.c. of water, placing the crucible in the ammonium carbonate solution contained in a small casserole. Warm the casserole slightly to hasten matters. Keep it covered with a watch glass to prevent loss during heating. (Use a casserole if a platinum dish cannot be had.) Filter, adding a little paper pulp. Wash with water containing ammonium carbonate until the washings are no longer milky when acidulated with a few drops of hydrochloric acid and tested with barium chloride. Then wash 10 times more. Ignite and weigh in the same crucible, and deduct the residue, which consists of all of the  $\text{SiO}_2$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , from the  $\text{WO}_3$ , etc., and calculate to percentage. The residue of  $\text{SiO}_2$ , if not pure white, is evaporated with hydrofluoric and sulphuric acid in the usual way, and the loss of weight constitutes the silicon present in the steel when multiplied by 47.02 and divided by the weight taken for analysis.

† The *sulphur* in such steels should be obtained by fusing 2

\* See bottom of page 72 relative to iron in sodium carbonate used to make the fusion for the removal of the iron.

† Read page 102 on sulphur in chrome-tungsten-vanadium steels.

grams of thin drillings with 20 grams of sodium carbonate and five grams of potassium nitrate. Dissolve in water, filter, wash, roast, fuse again, acidulate with HCl, evaporate combined filtrates to dryness twice, filter after each evaporation, washing with 1 : 20 HCl; precipitate the filtrate with barium chloride and finish as in gravimetric sulphur in steels. Make blank determination on like amount of the flux and acids, proceeding exactly as in actual analysis, and deduct the sulphur found from that found in the fusion of the steel. Multiply the weight of barium sulphate less that found in the blank by 13.73, and divide by the weight of sample taken for analysis to obtain the per cent of sulphur. The sulphur can also be obtained by direct solution in nitric acid, in all steels that will dissolve in it. Finish as in plain steel.

*Manganese.* Proceed as for manganese in steel when chromium is *present*, digesting the sample thoroughly with the mixture of acids as given, but omit the use of zinc oxide unless chromium be found. (See page 15.)

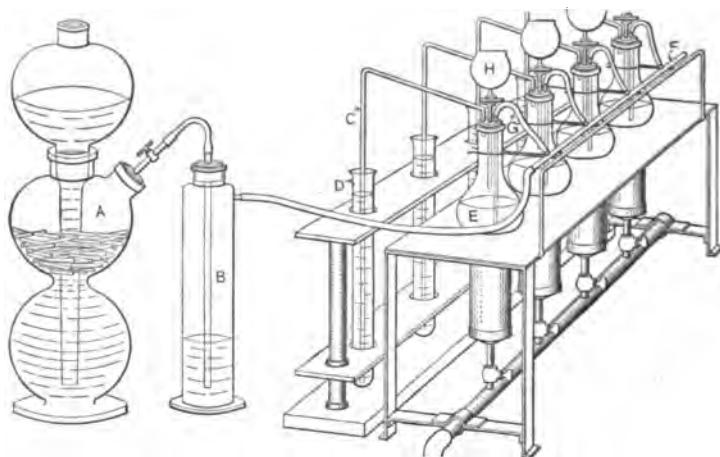
**THE GRAVIMETRIC DETERMINATION OF SULPHUR IN  
CHROMIUM-TUNGSTEN-VANADIUM STEEL  
WITHOUT A FUSION.**

Dissolve 4 or 5 grams of drillings in 200 c.c. of conc. nitric acid mixed with 100 c.c. of conc. hydrochloric acid using an 800 c.c. beaker. After the first action is over place the beaker on a graphite bath (see page 415) and heat without boiling. Stir the residue off the bottom of the beaker at intervals of a half hour. If, after an hour and a half of this digestion with the mixture of acids, the residue on the bottom of the beaker is not a clean yellow but still looks dark, especially in the layer touching the glass, then a fresh mixture of equal quantity should be poured into the beaker and the stirring and digestion continued until the entire insoluble portion is a clear, bright yellow, putting in a third mixture if necessary. The decomposition having been effected, the contents of the beaker are transferred

to a 600 c.c. casserole and evaporated on the graphite. Before the transfer to the casserole is made, 2 grams of sodium carbonate are added to the solution and stirred in well. This is to form with the sulphuric acid present sodium sulphate. Evaporate to dryness. Cool; add 100 c.c. of conc. HCl; cover; heat until all but the yellow residue of tungstic acid is in solution; evaporate again to dryness; dissolve as before with 50 c.c. of HCl and evaporate to 20 c.c. Add to the cool solution, 150 c.c. of water; heat and stir; add paper pulp and filter; wash with 1 : 40 HCl; add 20 c.c. of cinchonine solution and let stand for several hours, preferably until the next day to remove the last traces of metatungstic acid; filter; wash with cinchonine water (5 c.c. of cinchonine solution to 500 c.c. of water) 20 times. Heat the filtrate and washings to boiling and precipitate the sulphuric acid formed with 25 c.c. of a saturated solution of barium chloride and finish the determination as in plain steels, page 274. This method is of course applicable to plain chromium steels and nickel steels which give low results with the ordinary evolution method as given for plain steels, when several per cents of either or both of these elements are present. The cinchonine solution referred to is given on page 109. Run blanks repeating every operation and deduct the sulphur so found.

#### THE EVOLUTION APPARATUS FOR THE DETERMINATION OF SULPHUR IN PLAIN CARBON STEELS.

The bulb funnel referred to on page 269 is shown at *H* in Fig. 2. At *D* the thick wall, 10 × 1 inch, containing the ammoniacal cadmium chloride solution is given. The tube *F* with its four branches distributes the hydrogen to each dissolving flask *E*. On each branch a screw pinch cock, not shown in the cut, is located at the point *G* to shut off the hydrogen from any one flask *E*. The delivery tubes are as shown at *C*.



\* FIG. 2.

**THE DETERMINATION OF SULPHUR IN ALLOY STEELS BY  
HEATING THE INSOLUBLE RESIDUE TO BRIGHT REDNESS  
IN A STREAM OF ACID CARRYING HYDROGEN.**

In 1909 the writer in the first edition of this book, see pages 53 and 273, called attention to the fact that only a portion of the sulphur is obtained by the evolution as ordinarily applied to plain carbon steels. In some highly alloyed steels, notably the chrome-tungsten steels, as little as one-twenty-fifth of the true sulphur is so found. The writer has an experimental steel containing 0.250 per cent sulphur that shows but 0.010 per cent sulphur by the ordinary evolution method as given for plain carbon steels. This steel contains about 3 per cent chromium and 17 per cent tungsten and 0.49 per cent carbon.

The writer tried many schemes to overcome the failure of the evolution methods with no particular success until the autumn of 1911 when the following plan was worked out which gives practically all of the sulphur by evolution as hydrogen sulphide.

\* Designed some years ago by Dr. E. S. Johnson.

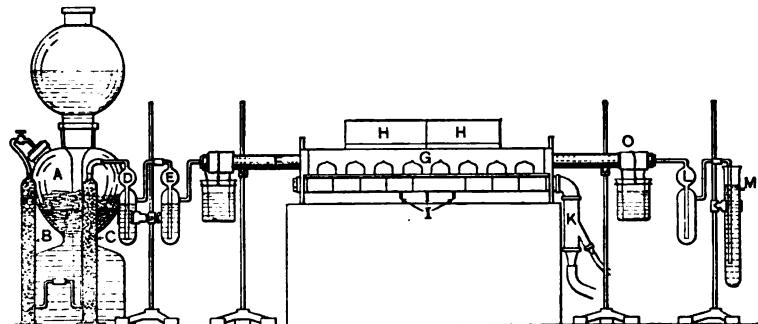


FIG. 3.

*Method.*

From 1 to 5 grams of steel, depending on the amount of sulphur present, are dissolved, exactly as given on pages 269 to 271 and the sulphur so obtained is determined. The insoluble residue is filtered off onto the same kind and size of filter as was used to retain the cadmium sulphide, see page 270. Any of the insoluble black carbide adhering to the walls of the flask *E*, Fig. 2, is removed by shaking around in it a small wad of filter pulp. The total insoluble residue is then placed in a  $15 \times 120$  mm. clay boat and shoved into the tube *F*, shown in Fig. 3. The present apparatus differs from the original one in that a quartz tube, having a tapered outlet of the same design as illustrated for carbon combustions on page 244, is now used. The outlet end being tapered has no rubber stopper so that the tube *L* is connected with the outlet of the evolution tube with a short piece of rubber tubing instead of a rubber stopper. The rubber stopper was extremely unsatisfactory as it always gave more or less sulphur. It was found very important to avoid all cooling at the outlet as low results were obtained when the outlet end was kept cold with wet wrappings, hence this end of the evolution tube was allowed to get quite warm but not hot enough to decompose the sulphur in the rubber tube connecting with *L*, and all cooling devices were omitted from the outlet *O* but rigidly adhered to at the inlet end near *F*. The Kipp *A* contains the stick zinc and 1 : 1 HCl. It is a 2 liter size. A

smaller one does not give enough pressure. *B* is filled with anhydrous calcium chloride and layers of cotton. *C* is similarly filled with pieces of stick KOH. *D* contains a saturated solution of mercuric chloride, to the depth of 1 inch, as a further guard against sulphur. *E* contains a  $1\frac{1}{4}$  inch layer of conc. HCl to saturate the hydrogen from *A* with HCl just before it enters *F*. The tube *E* should be refilled every other time it is used. The tube *L* is empty and is used as a trap for tarry matter, water and acid coming from *F*. *M* contains the ammoniacal solution of cadmium chloride of the same strength as used in ordinary evolutions. As stated the total insoluble residue is shoved into *F* which should be nearly cold or at least not hot enough to cause hydrogen to explode. The boat is pushed into the hottest part of *F* or to the location *G*. The furnace *G* is the same one as used for carbon determinations with air blast and gas. This type is better adapted for this work as it will cool quickly and heat up in a few minutes. Only the shutters in the middle of the furnace are opened as it is not desirable to heat the entire furnace for fear of burning the rubber connection with *L*. As soon as the boat is in place the stopper carrying *E* is inserted tightly into *F* and the stream of hydrogen is started through the apparatus. After the hydrogen has passed for about 20 minutes the burner is lighted and a sufficient amount of gas and air blast are applied to bring the tube up to a yellow heat in about ten or fifteen minutes. The passage of the gas at this temperature is continued for a half hour. Then the rubber connection with *L* is pinched tight and a freshly filled tube of the cadmium salt is substituted at *M*. The first tube holds almost all of the sulphur; if the conditions are just right but little sulphide forms in the 2nd *M*. Every half hour a fresh tube is put in at *M* until no further sulphide collects at *M*. The various *M* tubes are filtered through as in an ordinary evolution, beginning with the tube containing the least sulphide, and filtering all through the same paper.

The paper and the adhering sulphide are then finished as in plain steels as given on pages 269 to 271. This gives the major

part of the sulphur and is added to that obtained by the preliminary solution, to get the total evolved sulphur. In some steels the amount obtained in the preliminary solution may equal or exceed that obtained in the heated tube, depending both on the kind and the amount of alloying element present.

**STANDARDIZATION OF THE APPARATUS AND THE IODINE  
SOLUTION WITH BARIUM SULPHATE.**

The author decided that the best standardization medium would be c.p. barium sulphate and found that this salt is ideal for this work as its sulphur is readily converted under the conditions to hydrogen sulphide. The freshly ignited salt is quickly weighed onto a filter paper that has been moistened with some of the solution of an alloy steel from which the insoluble residue has been filtered in order to imitate as closely as possible the conditions of an ordinary test. The filter and the barium sulphate are then put in a clay boat and shoved into the cold evolution tube and the process is then carried out as already outlined. The cadmium sulphide so obtained is titrated to get the sulphur value of the iodine standard. For the standardization it is convenient to weigh 0.020 gram of the barium sulphate. A blank is also put through by moistening a filter paper with the same filtrate as is used in the standardizations. As a check standardization, one can use 0.010 gram of the BaSO<sub>4</sub>. The blank is deducted and the number of c.c. of the iodine required to combine with hydrogen sulphide evolved from the barium salt is divided into the sulphur content of the barium sulphate used. For example suppose it is found that a blank determination put through every operation consumed 2.4 c.c. of iodine and that 0.020 gram of the sulphate produced enough sulphide and other products from the filter and reagents to consume 25.8 c.c. Then since barium sulphate contains 13.73 per cent sulphur,  $0.020 \times 0.1373$  divided by 23.4 equals 0.0001173, or 1 c.c. of the standard iodine equals 0.0001173 gram of sulphur under the conditions as given.

## CHAPTER IV.

### PART IV.

#### ANALYSIS OF LOW PER CENT TUNGSTEN STEELS.

WHEN tungsten, phosphorus and silicon are wanted in steels that contain from 3.0 to 3.5 per cent tungsten and less than 1 per cent chromium, dissolve 3 grams in 60 c.c. of 1.20 nitric acid in a No. 5 dish. Evaporate to dryness. Ignite to dull red. Cool and dissolve in concentrated hydrochloric acid, and finish as given under the analysis of high chromium-tungsten steels when silicon and phosphorus are wanted.

#### ANALYSIS OF ALL TUNGSTEN AND CHROME STEELS WHEN CHROMIUM AND TUNGSTEN, ONLY, ARE ASKED FOR.

(*Third Method for Tungsten in Steel.*)

Dissolve 2 grams of sample in 30 c.c. 1 : 3 sulphuric acid. Heat until all action is over. Add 60 c.c. 1.20 nitric acid and digest at just below boiling until the residue in the 400 c.c. beaker is a clear yellow free of black particles. Dilute to 200 c.c. with water, and boil for 20 minutes. Add some paper pulp, filter, and wash free of iron test with dilute sulphuric acid. Dilute the filtrate to 500 c.c. and mix. From this solution fill a 250 c.c. flask to the mark.

*First Portion.* Precipitate the remaining tungstic acid from this portion with cinchonine. Wash it free of iron test with water containing cinchonine solution. Ignite it. Weigh and fuse with twenty times its weight of bisulphate of potassium. Obtain the amount of pure  $\text{WO}_3$  as given under bisulphate fusion; see pages 68 and 101. Multiply the weight of  $\text{WO}_3$  by 2. Iron can also be removed by sodium carbonate fusion. See page 72. The main tungsten precipitate is ignited, weighed

and purified in the same manner. The weight of  $\text{WO}_3$  thus obtained is added to twice the weight of the  $\text{WO}_3$  obtained by the cinchonine. This sum is multiplied by 79.31 and divided by the weight taken for analysis to obtain per cent of tungsten.

*Second Portion.* Finish this for chromium as given under determination of chromium in chromium-vanadium steel, pages 7 and 30. If the chemist prefers to obtain the chromium by a separate analysis, he can get the total tungsten by one operation. The entire filtrate from the main tungsten residue is precipitated, without dividing it, by cinchonine. This precipitate is burned off with the main residue. The combined residues which constitute the total tungsten from 2 grams of sample are then freed from impurities in the usual way with bisulphate or sodium carbonate, and the total weight of pure  $\text{WO}_3$  is multiplied by 79.31 and divided by the weight taken for analysis to obtain the per cent of tungsten. If the iron oxide is removed by sodium carbonate the silica is first removed by evaporation with hydrofluoric acid and sulphuric acid as given on page 72. The oxides are ignited, weighed, and then the iron is removed by the carbonate fusion.

#### CINCHONINE SOLUTION.

Dissolve 25 grams of cinchonine in 200 c.c. of 1:1 hydrochloric acid.

Cinchonine precipitates tungsten almost instantly from hydrochloric solution. It precipitates molybdenum after considerable lapse of time, and then only partially. At least, the above statement regarding molybdenum is correct if the attempt is made in the manner as given for tungsten. This constitutes a distinct difference between these two elements.

#### ANALYSIS OF CHROME-TUNGSTEN-VANADIUM STEELS FOR CHROMIUM AND VANADIUM.

These elements are determined as in chrome-vanadium steels, boiling with sufficient excess of permanganate so that the tung-

sten residue looks brown from manganese oxide after twenty minutes' boiling. Filter on asbestos and finish as usual. (See pages 7 and 30.)

#### THE ANALYSIS OF CRUCIBLE SLAG FROM TUNGSTEN-VANADIUM-CHROMIUM STEEL.

*Tungsten Oxide and Silica.* Fuse 1 gram of the finely ground slag with a mixture of 10 grams of sodium carbonate and 2 grams of potassium nitrate in a platinum crucible. Dissolve the melt in a platinum dish in water and transfer the solution and the insoluble matter to a 600 c.c. casserole; acidulate with an excess of HCl, about 75 c.c.; heat with the cover on until all effervescence is over, and evaporate to dryness on the graphite; heat with 30 c.c. of conc. HCl to dissolve the iron; then with 150 c.c. of water to dissolve the sodium salt; cool; add paper pulp; filter; wash with 1 : 40 HCl until free of iron test; hold this residue (A), as the main silicic and tungstic acids; the filtrate and washings from A are again evaporated to dryness; dissolved; filtered and washed as above; and the residue on the filter is designated as B. The filtrate and washings from B may still contain a little sodium metatungstate which is recovered by adding to the said filtrate and washings 10 c.c. of cinchonine solution; and, after stirring the same well, at least 4 hours are allowed to elapse before the tungsten cinchonate (C) is filtered out; washed with cinchonine water and burned off with B and A. The ash from A, B and C contains all of the tungsten and silica. The latter is removed by evaporation with 15 c.c. of HFl and 10 drops of conc.  $H_2SO_4$  and ignition at a low red heat. The difference between the weight of the ash from A, B, C, before this evaporation and its weight after the evaporation and ignition, is calculated to percentage of  $SiO_2$ . The residue remaining after the evaporation with HFl, etc. is fused with about twenty times its weight of sodium carbonate at a bright red heat for a half hour, or until all bubbling of  $CO_2$  is over; is dissolved in water; the insoluble residue is filtered out; thoroughly washed free of salt; ignited; weighed; and de-

ducted from the silica free weight of A, B, C. The remainder so obtained is figured to percentage of  $\text{WO}_3$ .

*Oxides of Calcium, Magnesium, Manganese and Iron.* Fuse 1 gram of the slag as above and proceed as directed up to the point where the filtrate and washings from B are obtained which will contain all of the Ca, Mg, Fe and Mn except a small amount remaining with the A and B. Fuse the ash from A and B with sodium carbonate as above, obtaining the water insoluble residue which, after being thoroughly washed, is dissolved in HCl and added to the main filtrate from B. A double basic acetate separation of the iron from the manganese in this main filtrate is made as directed on pages 188 and 189. On the filter, after the second basic acetate separation, will be the iron, chromium, and aluminum, and some V. In the combined filtrates from the two basic acetate separations will be the manganese, calcium and magnesium, which are separated and determined in the same manner as given on page 65 under the heading "Oxides of Manganese, Calcium, etc.,," beginning at the stage where the combined basic acetate filtrates are made distinctly ammoniacal and the manganese is precipitated with ferricyanide of iron.

The acetates of iron, chromium, aluminum, titanium and part of the vanadium, if present, are ignited and weighed at constant weight as  $\text{Fe}_2\text{O}_3$  plus  $\text{Al}_2\text{O}_3$  plus  $\text{Cr}_2\text{O}_3$  plus  $\text{TiO}_2$  plus some  $\text{V}_2\text{O}_5$ . These oxides are fused with 20 times their weight of sodium carbonate intimately ground with twice their weight of potassium nitrate to render the mixture of oxides soluble in acid. After keeping the melt in a molten condition for 15 minutes, it is cooled and dissolved in water and acidulated with an excess of HCl; heated in the porcelain dish (to which the water solution of the fusion is transferred before the acidulation is made), until all effervescence is over; the cover is removed; more acid is added, if necessary, and all is concentrated until a complete solution of the oxides is effected. The solution is then diluted in a volumetric flask to 500 c.c. and 250 c.c. are converted into nitrates by evaporating twice to 20 c.c. with 50 c.c. additions of conc.

nitric acid. This nitric solution is analyzed for vanadium as in ferro-vanadium; the vanadium found is calculated to  $V_2O_5$ , multiplied by two and deducted from the total weight of the  $Fe_2O_3$  plus  $Al_2O_3$  plus  $Cr_2O_3$ , etc., above mentioned. The other 250 c.c. are transferred to a liter boiling flask and peroxidized to remove the chromium and any vanadium in the manner described on page 23, beginning at the point where the directions read to dilute to about 300 c.c., getting filtrates A and B and carrying out a third peroxidation obtaining a filtrate C, or until a filtrate is gotten that is free from any yellow color of chromium. The residue remaining on the filter after the final peroxidation will contain all of the iron except a film of the latter remaining in the peroxidation flask. The iron on the filter is dissolved off with 1 : 1 HCl and is combined with the small portion recovered from the flask by warming in it some 1 : 1 HCl. This total iron is free of chromium and vanadium and can be determined by reducing it with tin chloride as in iron ores or it can be converted to sulphate and reduced with zinc or aluminum and titrated with permanganate. The combined filtrates A, B and C contain all of the Al and Cr in one-half of the original 1 gram weight. The Al can be removed from the combined filtrates, after first boiling them for ten minutes and then adding 1 : 1 HCl slowly and with rapid stirring, until turmeric paper no longer *immediately* changes to even a faint brown tint when dipped into the solution being neutralized. When the turmeric fails to change at once the solution is still alkaline enough to prevent any redissolving of the aluminum. The aluminum can then be filtered out and determined as given on page 19. The filtrate from the aluminum can be reserved for the chromium but the author prefers to determine the chromium on a separate sample. The iron found as above is calculated to FeO by the factor 1.286 and multiplied by 2 being one-half the sample.

*Chromium Oxide and Vanadium Oxide.* Fuse 1 gram of the ground slag in an iron crucible with 8 grams of sodium peroxide; dissolve out the fusion in water and boil for ten minutes in a

casserole; acidulate with 150 c.c. of 1 : 3 sulphuric acid; boil with an excess of potassium permanganate and finish for chromium and vanadium as in steels. In order to fix the proper blank for the vanadium titration and to check the chromium determination, 330 mgs. of potassium dichromate and 60 mgs. of vanadium pentoxide of 99.7 per cent V were fused in the same way as the slag and put through all of the operations. It required 132.6 c.c. of the double sulphate standard to react with the chromium; therefore  $0.330 \times 0.3535$  divided by 132.6 equals 0.00088 gram, or the value of the sulphate standard in chromium per c.c. The vanadium added, or  $60 \times 0.997$ , equals 0.0598 gram of  $V_2O_5$ . The percentage of V in the pentoxide being 56 per cent, there was present in the standard mixture  $0.56 \times 0.0598$ , or 0.0335 gram, V; 1 c.c. of the sulphate equals 0.00254 gram of V; therefore it will require 13.2 c.c. of this standard to equal 0.0335 gram of V. Now by actual titration 17.0 c.c. of the sulphate were used to obtain the blue end point in the second part of the titration made after the addition of the ferricyanide as in steels; (see page 40) hence the blank to be applied to the analysis of the tests of the slag should be 17.00 c.c. less 13.20 c.c. or a blank of 3.8 c.c. A mixture of 380 mgs. of  $K_2Cr_2O_7$  and 80 mgs. of  $V_2O_5$  put through the fusion and all of the above operations gave a chrome value of 1 c.c. of the standard equals 0.00088 gram of Cr and a V blank of 4.0 c.c. The average blank is, therefore, 3.9 c.c. In this particular slag by the above method 2.90 per cent V and a check result of 2.92 per cent V were found, which multiplied by the factor of 1.627 gave a value in  $V_2O_4$  of 4.71 per cent. The chromium found, using the above factor of 0.00088, was 11.76 per cent Cr and a check result of 11.88 per cent Cr giving an average of 11.82 which multiplied by the factor 1.461 equals 17.26, or the percentage of  $Cr_2O_3$  in the slag.

*Aluminum.* Having found the total iron by doubling that found in the 250 c.c. portion, it can also be calculated to  $Fe_2O_3$ ; to the ferric oxide add twice the vanadic oxide found in the other 250 c.c.; to this sum add the chromic acid found in the

separate portion; deduct the total of the three oxides from the total of the oxides of iron, chromium, aluminum and vanadium (being the portion of the vanadium that may be carried along with the other oxides) and the remainder is calculated to percentage as  $\text{Al}_2\text{O}_3$  plus any titanic oxide or phosphoric acid that may be present. The aluminum free from any titanium can be obtained by rendering the combined filtrates A, B and C neutral to *immediate* reaction with turmeric paper as given on page 24.

*Phosphoric Acid.* This acid will be also in the filtrates A, B and C and can be obtained therefrom as given on page 27.

*Manganese Oxide.* As previously stated the manganese is separated from the calcium and magnesium by the author's method of precipitating it from the combined filtrates from the basic acetate separation of the aluminum, iron and chromium, after rendering the combined filtrates distinctly ammoniacal. After thoroughly washing the ferricyanide precipitate with ammonium nitrate and weak ammonia wash, it is ashed in a porcelain crucible; dissolved in conc. HCl; evaporated to fumes with 40 c.c. of 1 : 3 sulphuric acid, dissolved by first boiling it with as little water as possible; and heating further with 1.20 nitric acid. The solution is then transferred to a 500 c.c. volumetric flask and diluted to the mark with 1.20 nitric acid. 25 and 50 c.c. portions are then analyzed for manganese as in steel. If the manganese by this method is found to be in excess of 5.00 per cent it is more reliable to use the method given for high manganese on page 188, or to analyze the above HCl solution for manganese as given on pages 201 and 202. The metallic manganese so found is calculated to MnO by multiplying it by the factor 1.291.

#### ANALYSIS FOUND.

	Per cent.		Per cent.
MnO.....	7.45	CaO.....	2.27
FeO.....	14.53	MgO.....	0.98
$\text{Al}_2\text{O}_3$ , etc.....	9.88	$\text{WO}_3$ .....	1.00
$\text{Cr}_2\text{O}_3$ .....	17.28	$\text{SiO}_2$ .....	41.78
$\text{V}_2\text{O}_4$ .....	4.71		

## CHAPTER V.

### PART I.

#### MOLYBDENUM POWDERS.

##### CARBON.

CARBON is obtained by direct combustion in a stream of oxygen, using the electric furnace with temperature between 900 and 950 degrees Centigrade. Decarbonization takes about a half hour. Use some red lead when the silicon content is high; two grams of the former per gram of Mo.

*Phosphorus.* If any molybdic acid separates out during the course of a determination of phosphorus as in steels, it is certain to carry phosphorus out with it as phospho-molybdic acid, in the same way that tungsten does. In such cases, dissolve the ferro or powder in a mixture of equal parts of conc. HCl and HNO<sub>3</sub>. Take 0.813 gram of the sample; dissolve it in 100 c.c. of the mixture; heat until all action is over; add 100 c.c. of conc. HCl; heat with the cover on until action is over and evaporate to 25 c.c. Dilute to 400 c.c. and remove the bulk of the molybdenum with H<sub>2</sub>S. Filter; wash; and evaporate the filtrate and washings to 20 c.c. Add 100 c.c. of conc. nitric acid; heat with cover on until action is over and evaporate to 25 c.c. Transfer to a 150 c.c. beaker; dilute to 40 c.c.; boil with a slight excess of KMnO<sub>4</sub> and finish as in phosphorus in steel.

##### SILICON.

Dissolve 1.5 grams in 60 c.c. 1:20 nitric acid. Add 120 c.c. of 1:3 sulphuric acid. Evaporate in a porcelain dish on graphite or sand bath to thick white fumes of sulphuric anhydride. Cool and add 80 c.c. 1:1 hydrochloric acid. Boil five minutes. Cool again and add 50 c.c. of water. Mix in some paper

pulp and filter on an 11 cm. double ashless filter. Wash free from iron test with 1 : 10 hydrochloric acid. Then wash free from chloride test with distilled water. Ignite in a platinum crucible at the faintest red heat until white. Weigh and evaporate with hydrofluoric acid and a few drops of sulphuric acid. Ignite again at lowest visible redness. Calculate the loss of weight as usual to silicon.

#### MOLYBDENUM.

##### *First Method.*

Fuse 0.500 gram of finely ground powder with twenty times its weight of sodium carbonate plus 2 grams of potassium nitrate. Heat cautiously until the fusion is free from black particles. Dissolve the melt in a platinum or porcelain dish (platinum preferred) with water. Remove the platinum crucible from the dish and rinse it off carefully, allowing the washings to run on the filter through which the water solution is to be poured. Mix the water solution of the fusion with a little paper pulp and filter it through the filter aforesaid. Wash the residue forty times with dilute sodium carbonate water. The residue on the filter contains all of the iron and copper present in the metal, a little platinum oxide from the crucible, and a little molybdenum.

The filtrate and washings are transferred to an 800 c.c. beaker. Two grams of tartaric acid are added. The solution is acidulated with sulphuric acid in *slight* excess. The acidulated solution is heated for twenty minutes to expel the major portion of the carbon dioxide. It is then cooled; three drops of phenolphthaleine solution are added. (See Phosphorus in Steel, p. 264.) A rather concentrated solution of sodium hydroxide is added until one drop produces a pink color. Next add 1 : 3 sulphuric acid until one drop causes the solution to become colorless. Dilute to 700 c.c. with water. If the attempt be made to precipitate molybdenum, in too acid a solution, by hydrogen sulphide, the former is partially reduced to a blue

oxide and partially precipitated as sulphide. To avoid this highly undesirable condition it is merely necessary to keep the solution but very slightly acid until it is well saturated with H<sub>2</sub>S. It then turns to a deep orange colored fluid from which the molybdenum is quickly precipitated, by the addition of 6 or 7 c.c. of 1:3 sulphuric acid, as a brown sulphide. Pass the gas for thirty minutes longer. Add paper pulp to the beaker, mixing it well with the sulphide just before passing the gas for the half hour as directed. In this way the precipitation is rapid. The sulphide can be filtered and washed quickly. It is washed with H<sub>2</sub>S water containing 2 drops of 1:3 sulphuric acid per 500 c.c. of wash water. Give the sulphide forty washings, permitting each washing to drain off thoroughly before the succeeding one is applied. The sulphide is then roasted just below redness in a platinum crucible. The contents of the crucible can be ignited without loss of molybdenum trioxide, but the crucible must not be allowed to exceed the faintest visible redness. The MoO<sub>3</sub> usually burns to a brownish white residue, owing to traces of impurities.

After weighing the oxide it is extracted with 1:1 ammonia (11.50 per cent) on the water bath until there remains but a small residue, consisting of traces of iron and some silica. This is mixed with a little paper pulp, filtered and washed thoroughly with dilute ammonia water.\* It is ignited, weighed, and its weight is deducted from the first weight of the MoO<sub>3</sub>. The remainder is multiplied by 66.66 (or  $\frac{2}{3} \times 100$ ) and divided by the weight taken for analysis to obtain the per cent of molybdenum in the sample. The filtrate and washings from the sulphide precipitation should always be tested by passing H<sub>2</sub>S through it for an hour more to make sure that no further precipitation of molybdenum sulphide will occur. If the directions as given are carefully followed, no molybdenum will be found at this point.

\* If this filtrate and washings are blue estimate the copper therein with KCN as in steels, page 150; calculate the copper found to CuO and deduct the result from the weight of the impure Mo<sub>3</sub>.

*Second Method.*

Completely soluble molybdenum can be examined for molybdenum as follows: Dissolve 0.400 gram of fine ground sample in 30 c.c. of 1.20 nitric acid. Cool and add 2 grams of tataric acid. Then add an excess of ammonia. Drop in 1:3 sulphuric acid until the solution is just faintly acid. Dilute to 800 c.c.; precipitate with hydrogen sulphide; and finish for molybdenum as given in the first method.

## IRON.

The residue of iron, etc., remaining on the filter from the water solution of the sodium carbonate and niter fusion is dissolved off with a little hot 1:1 hydrochloric acid. The filter is washed free from iron test. This filtrate and washings are almost certain to contain some molybdenum. (The writer has found molybdenum with the iron, even after it has been fused a second time with sodium carbonate.) Add dilute ammonia to the solution a drop at a time until the iron hydroxide appears. Then add sulphuric acid (1:3) until the iron precipitate just dissolves. Dilute to 300 c.c. with water. Pass H<sub>2</sub>S. The small quantity of molybdenum quickly separates. It is filtered out and washed in the same manner as the main sulphide precipitate. Ignite this sulphide to oxide, weigh it, extract it with ammonia in the same way as the main oxide. Filter out the insoluble matter, and wash it with dilute ammonia. Ignite it, weigh it, and deduct the weight from the first weight; calculate the remainder to Mo, and add it to the principal part of the molybdenum found. The filtrate and washings from the small sulphide precipitate contain all of the iron which can be determined by evaporation to a small volume with a slight excess of potassium chlorate. One or two grams should suffice. Then add an excess of 1:3 sulphuric acid and evaporate to thick, white fumes of sulphuric anhydride. Dilute with water. Reduce with zinc oxide or metallic aluminum, and finish by titration with permanganate solution as in the determination of iron in ferro-vanadium. (See page 28.)

## TUNGSTEN.

Evaporate the filtrate and washings from the main sulphide precipitate obtained by the first method to moist dryness. Add 100 c.c. of conc. nitric acid. Heat with cover on until all action is over. Remove the watch glass from the casserole and evaporate again to moist dryness. Add water; heat until all salt is in solution; filter out the insoluble residue; wash it free from salts with 1 : 20 hydrochloric acid. This will take about forty to fifty washings. Evaporate the filtrate and washings again to moist dryness, and add 100 c.c. of conc. hydrochloric acid. Heat with the cover on as before, and evaporate a third time. Add water; heat; \* filter; wash with 1 : 20 hydrochloric acid, and add the washed residue to the first one obtained after evaporating with nitric acid. Ignite and weigh as  $\text{WO}_3 + \text{SiO}_2$ . Finish as given for tungsten in steels.

## SULPHUR.

Fuse 2 grams with 20 grams of sodium carbonate and 4 grams of potassium nitrate. The fluxes are ground thoroughly together in an agate mortar. Heat until the melt is a clear light yellow, free of black specks. This requires but a few minutes. Dissolve the melt in water. Transfer it to a casserole. Acidulate with concentrated hydrochloric acid, and evaporate to dryness on the water bath. Add 40 c.c. of 1 : 1 hydrochloric acid. Heat with the cover on for a half hour. Add water and heat again. Filter and wash with 1 : 20 hydrochloric acid, forty times. Heat the filtrate to boiling, and precipitate with barium chloride solution, adding the latter in excess, about 50 c.c. of the saturated solution. Considerable molybdenum is precipitated with the barium sulphate. Filter, washing with water, only, until free from chloride test to insure removal of the excess of  $\text{BaCl}_2$ . Plug the end of the funnel with a rubber cap

\* Add 20 c.c. of cinchonine solution; warm for a short time to permit the precipitate to settle; wash it with a mixture of 50 c.c. HCl, 400 c.c. of water and 5 c.c. of the cinchonine solution. Read also page 125.

and fill it three-fourths full with 1 : 1 ammonia water (11.50 per cent) and keep covered for four hours, or longer if convenient. Then allow this fluid to drain off, and wash the residue with the 1 : 1 ammonia until 10 c.c. of the washings on being acidulated in a 254 by 25.4 mm. tube with hydrochloric acid, brought just to a boil with granulated tin (Do not continue to boil. See Qualitative Mo Test, page 2), cooled to room temperature and treated with 1 or 2 c.c. of KCNS solution, give no reddish coloration due to molybdenum. Ignite and weigh as BaSO<sub>4</sub> as in steels. Deduct a blank. It is always safer to fuse this BaSO<sub>4</sub> with sodium carbonate; dissolve the fusion in water; filter it; acidulate it with hydrochloric acid; and reprecipitate it with barium chloride as described under gravimetric sulphur in steels, page 275.

Even with all of the foregoing precautions, the author has found still 2 or 3 mgs. of Mo in the BaSO<sub>4</sub>. To correct for the Mo, fuse the impure BaSO<sub>4</sub> with 20 times its weight of Na<sub>2</sub>CO<sub>3</sub>; dissolve the melt in water; filter out the barium carbonate formed; wash 20 times with water; add a few drops of methyl orange to the filtrate and washings; then add 1:1 HCl until 1 or 2 drops of the acid turn the solution pink; then pass H<sub>2</sub>S until the small precipitate of molybdenum sulphide separates out well; wash the sulphide with H<sub>2</sub>S water until free of chlorides; ignite it at the faintest redness; weigh it; and deduct the weight from that of the impure BaSO<sub>4</sub> and calculate the remainder, as usual, to sulphur.

#### MANGANESE.

Proceed as in steels or ferro-vanadium, dissolving the powder in 1.20 nitric acid.

#### COPPER.

Nitric acid solutions of molybdenum are precipitated but slightly, even after one hour's standing, by potassium ferrocyanide. This reagent affords a rapid means of determining the amount of copper that may be present in the molybdenum. Dissolve 1 gram of sample in 30 c.c. 1.20 nitric acid. Add

ammonia until the iron hydroxide forms. Then add sulphuric acid (1 : 3) a few drops at a time until the hydrate of iron is just dissolved. Now precipitate the copper with 20 c.c. of the same potassium ferricyanide solution used to separate copper in ferro-vanadium. (See page 149.) If the copper in solution is likely to exceed 10 mgs., then add an additional 2 c.c. of the ferricyanide solution for every milligram of copper in excess of 10 mgs. Finish as given in the author's method for copper in steel, page 149. The analysis of ferro-molybdenum is similar to that of the powders.

## TYPICAL ANALYSES.

		Carbonless.
	Per cent.	Per cent.
Carbon.....	4.60	0.07
Manganese.....	0.03	0.18
Phosphorus.....	0.029	0.059
Sulphur.....	1.02	.....
Silicon.....	0.50	2.88
Molybdenum.....	90.00	92.50

## CHAPTER V.

### PART II.

#### THE ANALYSIS OF FERRO-MOLYBDENUM.

DISSOLVE 0.4 and 0.5 gram for a check in 50 c.c. of 1.20 nitric acid to a clear solution. Dilute to 200 c.c.; add a considerable excess of 1 : 1 ammonia and precipitate the iron. Redisolve this iron in 50 c.c. of 1 : 1 HCl; reprecipitate the iron again, washing as before with dilute ammonia wash. The iron hydroxide is dried; ignited; and weighed as  $\text{Fe}_2\text{O}_3$  + some  $\text{MoO}_3$  and a little  $\text{SiO}_2$ . The residue in the crucible is dissolved in HCl; the silica is filtered out; washed; weighed and deducted from the total weight of the oxides of iron, etc. The filtrate from the silica is made nearly neutral and the molybdenum therein is precipitated with  $\text{H}_2\text{S}$  in hot solution; filtered out; washed with  $\text{H}_2\text{S}$  water; ignited at a very low red heat; weighed and deducted from the iron oxide, etc., giving a remainder consisting of  $\text{Fe}_2\text{O}_3$  plus any phosphoric acid that may have been carried out with the iron oxide. This phosphoric acid can be found by evaporating the filtrate from the above molybdenum sulphide to low volume; convert to nitrates and finish the phosphorus as in steels. The phosphorus so found is calculated to  $\text{P}_2\text{O}_5$  and deducted from the weight of the  $\text{P}_2\text{O}_5$  plus  $\text{F}_2\text{O}_3$ , leaving a remainder that can be calculated to metallic iron. This phosphorus is not necessarily the total phosphorus. The latter can be determined on a separate portion as described under Phosphorus in Molybdenum Powder.

The main portion of the molybdenum is contained in the two sets of filtrates and washings from the precipitation and the reprecipitation of the iron by ammonia as given above. These filtrates and washings are combined; made slightly acid with HCl and the Mo is separated with  $\text{H}_2\text{S}$ ; washed; ignited and

weighed as  $\text{MoO}_3$  plus any little silica present which is removed by dissolving the  $\text{MoO}_3$  in conc. ammonia and warming until only a small floating residue remains which is filtered out; washed with ammonia water; ignited; weighed; and deducted from the first weight of the main  $\text{MoO}_3$ . The remainder plus the  $\text{MoO}_3$  found with the iron, as already described, constitutes the total  $\text{MoO}_3$  which is calculated to Mo by the factor 0.6666.

*Silicon.* This element can be determined on the same portion as is used for the molybdenum if the nitric acid solution is taken to dryness on the graphite bath. Do not ignite the dish over a bare flame as in tungsten as there is danger of loss of the Mo by volatilization. Dissolve the dry residue in 50 c.c. or more, if necessary, of conc. HCl; dilute; filter; wash with dilute HCl; wash until the residue on the filter no longer gives a test for iron; evaporate the filtrate and washings again to dryness; dissolve; filter; wash as before; combine the two filters from the first and second evaporation; ignite the same at a very low red heat and weigh as  $\text{SiO}_2$  plus a little  $\text{MoO}_3$ . For close work this silica should be fused with 10 times its weight of sodium carbonate; the fusion dissolved in HCl and evaporated twice to dryness as before, finally weighing as pure silica. The filtrate from the second evaporation to dryness in the presence of the main iron and Mo can be combined with the filtrate and washings from the evaporation of the acidulated sodium carbonate fusion of the impure silica. The combined filtrates contain the total iron and Mo and can be analyzed for these elements as already given under Ferro-Molybdenum.

The carbon, manganese and tungsten are determined as given for Molybdenum Powders.

#### RESULTS OBTAINED ON A HIGH CARBON TYPE.

	Per cent.		Per cent.
Carbon.....	3.66	Silicon.....	0.86
Manganese.....	0.13	Iron.....	23.26
Phosphorus.....	0.035	Molybdenum.....	71.30

## THE ANALYSIS OF FERRO-MOLYBDENUM-TUNGSTEN.

*Tungsten, Phosphorus and Silicon.* Dissolve 1 gm., and  $1\frac{1}{2}$  gms. for a check, in 50 c.c. of 1.20 nitric acid in a No. 5 porcelain dish; evaporate dry but do not ignite with a bare flame. Redissolve with 100 c.c. of conc. HCl; evaporate dry; dissolve in 50 c.c. of conc. HCl and evaporate to 20 c.c.; add 25 c.c. of water; heat 20 minutes; filter; wash with 1 : 40 HCl; evaporate the filtrate and washings to 10 c.c.; add 25 c.c. of water; heat and filter out any small residue of tungstic acid that may have separated out after this second evaporation. The filtrate and washings from this last evaporation are taken to 40 c.c. in a 150 c.c. beaker; heated to near boiling; removed from the fire and 50 c.c. of molybdate solution are added to precipitate the phosphorus which is then finished as in tungsten steel. (See page 100.)

The residues on the filters from the above first and second evaporation to dryness contain all of the tungsten, silicon and a little of the molybdenum. These papers are ignited at a low red heat until the carbon is gone; add 10 grams of anhydrous sodium carbonate to the ash and fuse to a clear liquid that no longer gives off any bubbles of CO<sub>2</sub>. Dissolve out this fusion; acidulate it with HCl and evaporate to dryness, after all effervescence and spraying are over, in the covered casserole. If the fusion is dissolved out in porcelain, the solution must be made acid with HCl as the dissolving of carbonate fusions with water alone in porcelain dishes causes the latter to be attacked and silicon results to be too high, especially if heat is applied to hasten matters.

After the evaporation to dryness the residue is redissolved in HCl; add water; filter out the tungsten; wash it as before; evaporate the filtrate and washings again to dryness; dissolve; filter; and wash. This second filtrate and washings will contain some tungsten which must be removed by cinchonine; heat the filtrate before adding the cinchonine; filter out the tungsten so precipitated; wash it with cinchonine water; combine this filter with the two residues obtained from the evap-

oration of the above fusion twice to dryness and burn all in a platinum crucible to a yellow residue free from the carbon of the filters; weigh it as  $\text{WO}_3 + \text{SiO}_2$ . Remove the silicon by the usual evaporation with  $\text{HfI}$  and  $\text{H}_2\text{SO}_4$ , calculating the loss of weight as the silicon of the alloy. The residue in the crucible is calculated to tungsten by the factor 0.7931.

*Molybdenum.* Fuse 0.5 gram of the finely ground alloy in a platinum crucible with an intimate mixture of 10 grams of sodium carbonate and 0.5 gram of niter until a quiet fusion is obtained and then continue to maintain the fusing temperature for 10 minutes more. Dissolve the fusion out in water; filter out the insoluble residue of iron and manganese; wash it with sodium carbonate water; ignite it; grind it in a small agate mortar; return the fine powder again to the crucible; clean the mortar by grinding it out with a little sodium carbonate; return this carbonate to the crucible; again grind some fresh carbonate in the mortar, and so on until the carbonate no longer shows a change of color when ground in the mortar. Grind 10 grams of carbonate with 0.200 gram of niter for this second fusion which is made and dissolved out as in the first fusion. The filtrates and washings from insoluble residues obtained after each fusion contain all of the molybdenum and tungsten from the alloy. The first filtrate and washings contain practically all of these elements. Add to it 2 grams of tartaric acid and 2 drops of methyl orange solution (1 gram of the methyl orange dissolved in a liter of water). Now add  $\text{HCl}$  until one drop just turns the solution pink. Pass  $\text{H}_2\text{S}$  through the solution when it will turn a deep red due to the combination with the  $\text{H}_2\text{S}$ ; the addition of a few drops of  $\text{HCl}$  will cause the molybdenum sulphide to then precipitate out promptly and perfectly after a thorough saturation with  $\text{H}_2\text{S}$ . The directions must be carefully followed for if the attempt is made to precipitate molybdenum from a solution containing much free acid, a blue filtrate is obtained which contains much of the molybdenum in a reduced form that is very unsatisfactory to handle, as explained on page 131. Wash the molybdenum sulphide, so obtained from both sets of

filtrates and washings, thoroughly with  $H_2S$  water; ignite it at a low red heat and weigh; dissolve this  $MoO_3$  in ammonia; filter the solution; wash the filter thoroughly with ammonia; ignite it; weigh it; deduct this weight from the first weight of the  $MoO_3$  and calculate the difference in weight to molybdenum by the use of the factor 0.6666.

*Iron.* The insoluble residue obtained from the second fusion with sodium carbonate and niter contains all of the iron free from tungsten and Mo and is especially convenient for the iron determination as the two latter elements must be separated before the iron can be determined. Dissolve this residue, after burning off the paper in the crucible in which the fusion was made, in conc. HCl; clean the iron stains from the crucible with this acid; precipitate the solution of the residue and the cleanings of the crucible with ammonia; redissolve; reprecipitate, and redissolve it again to remove any platinum; then reduce the solution with stannous chloride and finish for iron as in iron ore by titration of the reduced iron with potassium dichromate. (See page 367.)

*Sulphur.* Heat 2 grams and 3 grams for a check, of the powdered sample or drillings with 200 c.c. of conc.  $HNO_3$  in 600 c.c. beakers until red fumes are gone; add 100 c.c. of HCl and heat until all action is over and the insoluble portion is of a clear yellow color; transfer the solution to a casserole; add 2 grams of  $Na_2CO_3$  and evaporate to dryness; do not ignite; add 20 c.c. of conc. HCl; and heat until the insoluble matter is floatant; add 150 c.c. of water, and heat further; filter and wash with HCl water; evaporate the filtrate and washings again to dryness; redissolve; dilute; filter; and wash as before; precipitate the iron from the filtrate and washings with a slight excess of ammonia; filter out the iron hydroxide and wash it with water; dilute the filtrate and washings from the iron to 300 c.c.; add enough HCl to this filtrate and washings to just neutralize it, and then an excess of 20 c.c. of conc. HCl; dilute with water to 400 c.c.; heat to boiling; add 25 c.c. of a saturated solution of barium chloride; let the solution stand 12 hours. Filter off the barium sulphate

which is almost certain to contain considerable molybdenum. Wash this precipitate with water only; ignite it at a low red heat in a platinum crucible; moisten it with a drop or two of sulphuric acid to convert any barium sulphite formed by the reducing action of the burning filter paper; fuse this residue of barium sulphate and some Mo with 1 gram of sodium carbonate; dissolve the melt in water; filter out the barium carbonate; wash the filter thoroughly with water containing 5 grams of sodium carbonate to 500 c.c. of water. Add to the filtrate and washings 2 drops of methyl orange; then HCl until the solution just turns pink; then add an excess of 40 c.c. of 1 : 1 HCl and dilute to 400 c.c. with water. Heat to boiling and precipitate, as before, the sulphur present as barium sulphate. Finish from this point as given on page 120. Blanks should be run covering all operations and any sulphur, so found, deducted.

*The carbon and manganese* can be determined as in tungsten powder.

#### ANALYSIS FOUND.

	Per cent		Per cent
Carbon.....	1.84	Tungsten.....	10.02
Manganese.....	0.32	Molybdenum.....	42.66
Phosphorus.....	0.086	Iron.....	42.12
Silicon.....	1.85	Sulphur.....	0.14

## CHAPTER V.

### PART III.

#### THE DETERMINATION OF MOLYBDENUM IN MOLYBDENITE ORE.

THE finely ground sample is heated for a time with 100 c.c. of conc. HCl; and then with the addition of 4 grams of potassium chlorate, in 2 gram portions, until the smell of chlorine is gone. Add 150 c.c. of water, filter and wash. The free acid in the filtrate must be neutralized with 1 : 1 ammonia. Pass H<sub>2</sub>S until the molybdenum sulphide settles well in hot solution. Filter out the sulphide and wash it with H<sub>2</sub>S water containing a drop or two of 1 : 1 HCl. The molybdenum sulphide obtained at this point is dried and retained.

The filtrate and washings from the sulphide are tested with more H<sub>2</sub>S but none will be found if the conditions are correct, that is, the Mo should be precipitated from as nearly neutral a solution as possible. The insoluble residue from the original treatment with HCl and chlorate is burned off in a 30 c.c. platinum crucible at a very low red heat and, when the carbon of the paper is all gone, the ash is fused with 10 grams of sodium carbonate. Dissolve the fusion in a 600 c.c. casserole with 80 c.c. of conc. HCl. Clean the crucible with a little HCl and take the total solution to dryness. Redissolve by first heating with 20 c.c. of conc. HCl; add 150 c.c. of HCl; filter off the silica; wash with dilute HCl wash; evaporate the filtrate and washings again to dryness; take up; filter; wash as before; pass H<sub>2</sub>S through this last filtrate and washings to get the remainder of the molybdenum. Filter out the molybdenum found here; wash it as in the first precipitation; and combine it with the Mo found in the first instance. Test the filtrate and washings from this second H<sub>2</sub>S precipitation to make sure that all of the Mo has been precipitated.

The total sulphides of Mo are then burned at a very low red heat and finished as in molybdenum in steel.

## CHAPTER V.

### PART IV.

#### METHOD FOR TUNGSTEN AND MOLYBDENUM STEELS.

##### ABSENCE OF MOLYBDENUM.

(*Second Method for Tungsten in Steel.*)

DISSOLVE 2 grams of steel in a mixture of 30 c.c. of concentrated nitric acid and 30 c.c. of 1.20 specific gravity hydrochloric acid in a No. 5 porcelain dish. Keep at a digesting heat until the tungstic acid is a bright yellow. Agitate the solution frequently by stirring the sediment vigorously, but do not leave glass rods in the hot acid. Remove the former after each stirring, as tungstic acid attacks glass in hot acid solution, causing silicon results to be too high. When the tungstic acid is a clear yellow remove the lid and evaporate to 20 c.c. volume.\* Now add 100 c.c. of distilled water. Stir thoroughly. Remove stirring rod. Heat to incipient boiling for at least a half hour. Filter, adding ashless paper pulp. Wash with 1 : 20 hydrochloric acid until free of iron test. Ignite and weigh as  $\text{WO}_3 + \text{SiO}_2 + \text{Fe}_2\text{O}_3$ . Evaporate with hydrofluoric and sulphuric acids as described on page 72. Weigh as  $\text{WO}_3 + \text{Fe}_2\text{O}_3$ . The loss of weight here is part of the total silicon. This is the most rapid of the three methods for tungsten in steel.

Fuse the  $\text{WO}_3 + \text{Fe}_2\text{O}_3$  with 5 grams of sodium carbonate until molten. Keep molten for 20 minutes. Dissolve in a casserole with distilled water. Filter out the small residue of

\* At this point, in order to insure the complete removal of the nitric acid, it is better to carry this evaporation further until moist dryness is attained; then add 50 c.c. of conc. HCl and evaporate to 10 c.c., heating with the cover on the vessel, in case red fumes form on introducing the 50 c.c., until all danger of loss from spraying is over. Then evaporate to 10 c.c. as directed. "Now add 100 c.c. of distilled water," etc.

iron and wash it with water until free of carbonate. About forty washings will suffice. Ignite this residue in a weighed crucible, and deduct its weight from the weight of  $\text{WO}_3 + \text{Fe}_2\text{O}_3$ . The remainder is the pure  $\text{WO}_3$ , which, multiplied by 79.31 and divided by the weight taken for analysis, yields the per cent of tungsten. Read page 72 concerning iron in  $\text{Na}_2\text{CO}_3$ .

#### SILICON AND PHOSPHORUS.

If silicon and phosphorus are asked for, evaporate the filtrate and washings from the tungstic acid to 10 c.c. Add 50 c.c. conc. nitric acid and evaporate again to 10 c.c. Add 50 c.c. more of conc. nitric acid and evaporate to hard dryness. Ignite to dull red, and proceed as given on page 99 for the *balance* of the silicon and for the phosphorus.

#### IN THE PRESENCE OF MOLYBDENUM.

Proceed as in the absence of molybdenum to the point where the filtrate and washings from the tungstic acid have been obtained. Transfer the fluid to a 500 c.c. flask. Dilute to the mark with water. Mix thoroughly, and from this quantitatively fill a 250 c.c. flask.

Finish one portion for phosphorus and silicon as given in the absence of molybdenum. Calculate the phosphorus on the basis of one-half the original weight taken for analysis, that is, as though 1 gram were taken. The silicon obtained from this portion is multiplied by 2 and added to that obtained from the tungstic oxide. The total is calculated on a 2 gram basis.

The tungstic oxide, which always contains a little, and sometimes much, molybdic oxide, is ignited at the faintest red heat until yellow; weighed; the silica is removed from it by evaporating with hydrofluoric and a little sulphuric acid. The residue is then ignited at the lowest possible heat and weighed again. The loss of weight at this point is the silica that remained with the tungstic oxide.

The remainder is the  $\text{WO}_3$  plus some  $\text{MoO}_3$  and  $\text{Fe}_2\text{O}_3$ . The combined oxides are fused with 10 grams of sodium carbonate

for a half hour at a red heat with a Bunsen burner. The melt is dissolved in water; the iron is filtered out and washed with water. It is ignited; weighed; and the weight is deducted. The filtrate and washings are treated with 2 grams of tartaric acid; are acidulated very slightly with sulphuric acid; and the molybdenum is separated with  $H_2S$ . The  $MoS_3$  is ignited to oxide, and the weight of the oxide is deducted from the weight of  $WO_3 + MoO_3$ . The remainder is multiplied by 79.31 and divided by the weight taken for analysis to obtain the percentage of tungsten. See the directions for the precipitation of molybdenum as sulphide, given below.

As molybdic oxide sublimes at a bright red heat, hence the repeated caution not to ignite either it or the sulphide above the faintest suggestion of redness. A slight white fume rising in the crucible when heating the oxide at redness indicates loss of the latter. The  $MoO_3$  found with the tungstic oxide is calculated to Mo multiplying by 0.6666. This amount is added to twice the weight of Mo, in parts of a gram, found in the second 250 c.c. portion. The total is multiplied by 100 and divided by 2 to obtain the total per cent of molybdenum in the two gram sample.

The principal part of the molybdenum, obtained in the second half of the divided filtrate, is separated as follows: Add ammonia to it until a precipitate forms that no longer dissolves on stirring. Add 1 : 3 sulphuric acid until this precipitate *just* dissolves. Then saturate the *nearly neutral* solution with hydrogen sulphide, and obtain the molybdenum in this half of the divided filtrate. If the solution containing the molybdenum is too nearly neutral,  $H_2S$  causes only a deep red coloration in it; if the solution is too acid, the passage of the hydrogen sulphide results in a partial precipitation of the molybdenum together with a blue coloration. From the red solution the molybdenum is easily precipitated by a *very slight* addition of acid. Add the latter cautiously, a c.c. or two at a time, until the molybdenum begins to settle rapidly. Then pass  $H_2S$  a little while longer. If the  $H_2S$  has been passed through too acid a solution of molybdenum, with the resulting partial precipitation giving a blue

filtrate, the best thing to do is to begin the analysis over, giving proper attention to these details. The molybdenum can be completely precipitated, if the conditions are observed as here given, in a half hour's time with a rapid stream of  $H_2S$ .

#### VOLUMETRIC DETERMINATION OF MOLYBDENUM IN STEEL.

After weighing the molybdenum as oxide, the results so obtained can be checked as follows: Fuse the oxide with 5 grams of carbonate of soda. Dissolve the melt in about 50 c.c. of water in a dish. Filter the solution on a 7 cm. filter. Wash the latter thoroughly with sodium carbonate water. Evaporate the filtrate and washings to 50 c.c. Acidulate with 1 : 3 sulphuric acid, adding an excess of 100 c.c. Next add 1 c.c. of 1 : 1 hydrochloric acid after acidulation with sulphuric acid.

Place in the beaker a square inch of 1.7 mm. ( $\frac{1}{16}$  inch thick) aluminum foil with its corners bent at right angles. Heat the solution so as to maintain rapid action between the foil and the acid. In a half hour the reduction is *usually* complete.

Titrate with potassium permanganate standard until 3 drops of the latter render the solution a distinct pink, in the cold, for 1 minute. Remove the foil before beginning the titration, rinsing it with cold water. Heat a similar piece of foil for a half hour in a solution containing 5 grams of sodium carbonate acidulated with 120 c.c. 1 : 3 sulphuric acid. Add also 1 c.c. of 1 : 1 hydrochloric acid after acidulating with sulphuric acid. Titrate the blank exactly as given for the test. Deduct the c.c. of permanganate used by the blank from the amount required to oxidize the test, and multiply the remainder by 0.001925 to obtain the weight of molybdenum present in the sample. The permanganate standard is prepared by dissolving 1.86 grams of the salt in water and diluting the solution to 1 liter. Its value in metallic iron multiplied by 0.88163 equals its value in  $MoO_3$ . This method possesses no advantage over the ignition of the sulphide to oxide and weighing as such.

**WEIGHING OF THE MOLYBDENUM AS LEAD MOLYBDATE.**

After weighing as oxide, fuse the latter with 5 grams of sodium carbonate. Dissolve the melt in water. Filter it, washing thoroughly with sodium carbonate water. To the filtrate and washings add 2 or 3 drops of methyl orange. Now titrate the solution until it turns pink with 1:1 HCl. Add 1 c.c. in excess. Heat the solution to almost boiling. Add 30 c.c. of a filtered saturated solution of lead acetate in this manner: First add 20 c.c. and permit the precipitate to settle somewhat; then pour in the remaining 10 c.c., noting if there seems to be a further formation of the white precipitate. If more forms, add an additional 10 c.c., or 40 c.c. in all. Now add 50 c.c. of a solution of ammonium acetate.\* Stir the mixture thoroughly and allow the lead molybdate to settle for two hours. It is filtered, washed with hot water, and ignited at a low red heat until white. It is weighed and the weight multiplied by 0.2616 to reduce the weight to metallic molybdenum. Test the filtrate and washings with 10 c.c. of the lead acetate solution, and note if a further precipitation occurs in the course of an hour or two. This is a satisfactory method, as a check. The ammonium acetate solution is prepared by dissolving 500 grams of the crystals in 1000 c.c. of water.

\* Brearley and Ibbotson suggested the use of ammonium acetate at this stage.

## CHAPTER V.

### PART V.

#### DETERMINATION OF TIN AND BISMUTH IN PLAIN AND ALLOY STEELS.

DISSOLVE 2 grams of drillings by heating the same in a No. 5 porcelain dish on the water bath. After action with HCl is over begin to further attack the steel, if it contains large quantities of chromium and tungsten, by additions of potassium chlorate, 0.500 gram at a time at intervals of 30 minutes until the insoluble residue is bright yellow if tungsten be present. Heat until all smell of chlorine is gone. The sample is usually well decomposed when the amount of chlorate added equals about 2 grams. Now add 50 c.c. of water; heat for a half hour; filter out the insoluble residue and wash the same free of iron test with dilute HCl.

The filtrate and washings are made nearly neutral with ammonia and 20 c.c. of a cinchonine solution are added, if the steel contains tungsten, to remove the last traces of the latter. The solution is allowed to stand over night to make sure that all traces of tungsten are separated. The tungsten is then filtered out, and the filter is washed with cinchonine water as in the determination of tungsten. Any traces of tungsten remaining behind are very likely to contaminate the tin sulphide, obtained later. (This cinchonine solution is made by dissolving 50 grams of the latter alkaloid in 200 c.c. conc. HCl and 800 c.c. of water.)

The filtrate and washings from the cinchonine precipitation are diluted to 400 c.c. and hydrogen sulphide is passed until the mixture of sulphur and sulphides settle well in the hot solution. The sulphides are filtered off and washed with hydrogen sulphide water until free of ferrous iron test with ferricyanide of

potassium. This requires 50 washings. Two drops of the 1 : 1 HCl are put in 500 c.c. of this wash.

Burn off the mixture of sulphides at a very low red heat in a weighed porcelain crucible. The residue in the crucible may contain small amounts of oxides of copper, molybdenum, bismuth, iron and silicon besides the oxides of tin. The oxides are heated at a red heat for a half hour after the paper is all burned away. The total weight of the oxides is obtained and then the oxides are extracted with 20 c.c. of conc. ammonia to remove the molybdenum. The residue insoluble in ammonia is filtered off; washed with ammonia water; burned off as before; and is then heated with 1 : 1 HCl to remove the small amount of iron, copper and bismuth that may be present. Again the residue insoluble in the HCl is filtered off; washed; and weighed. This weight represents the tin oxide together with a little silica. To remove the silica the residue, after being weighed free of the iron, bismuth and copper, is transferred to a platinum crucible, moistened with 5 drops of the conc.  $H_2SO_4$  and evaporated to dryness with 5 c.c. of HFl to remove the silica. The crucible is then heated to redness again, cooled and weighed. The weight so obtained is calculated to metallic tin by multiplying by the factor 0.7887. A first class steel will not show by this method much over 0.050 per cent Sn. The author has repeatedly had the method tested by adding known amounts of tin to alloy steels; and has recovered the amounts added within a fraction of a milligram. It must be remembered, in this connection, that chloride of tin is volatile; for this reason the author never heats the samples above the water bath temperature during the decomposition with hydrochloric acid and chlorate.

In case it is desired to determine both tin and bismuth, it is better to separate these two elements, as given under the determination of Bi and Sn in tungsten powder, when much tin and bismuth are present, page 88, by the use of yellow ammonium sulphide and flowers of sulphur.

## CHAPTER VI.

### PART I.

#### ANALYSIS OF FERRO-CHROME, CHROME ORE AND CARBONLESS CHROME.

FERRO-CHROME and carbonless chrome usually dissolve completely in 1 : 3 sulphuric acid. The ferro should be ground as fine as possible. Carbonless chrome dissolves readily without grinding to any especial degree.

When a residue of a gritty or metallic nature remains after digestion with the dilute acid, it is filtered out, washed twenty times with 1 : 10 sulphuric acid, roasted, fused with twenty times its weight of sodium carbonate plus a fifth of its weight of potassium nitrate. The fusion is dissolved in water in a platinum dish, or porcelain one, and then poured into the main solution.

\* Dissolve from 0.3 to 0.4 gram of sample in 30 c.c. 1 : 3 sulphuric acid as described, fusing the residue if there be any. Add 60 c.c. 1.20 nitric acid, and treat exactly as stated for determination of vanadium in ferro-vanadium until the filtering through asbestos to remove the excess of manganese oxide has been accomplished. To the cold filtrate add from 1 to 2 c.c. of the ferricyanide indicator. Add also 50 c.c. of 1 : 3 sulphuric acid. Titrate at once with a standard solution of ferrous ammonium sulphate of double the strength of that used for vanadium work. When 3 drops of this standard produce a darkening of the green to a blue, after the entire disappearance of all red or yellow tints, the end point is reached.

#### STANDARDIZATION AND CALCULATIONS.

Dissolve 39.163 grams of ferrous ammonium sulphate in water; add 50 c.c. of 1 : 3 sulphuric acid; and dilute to 1 liter for standard. To standardize the ferrous ammonium sulphate

\* Use from 0.2 to 0.25 gram if Cr in the ferro is over 50 per cent Cr.

weigh into a 5 ounce beaker 0.500 gram of recrystallized c.p. potassium dichromate. Dissolve these crystals in a small quantity of water. Add to the water solution sulphurous acid until the chromate is entirely reduced to a dark green and smells distinctly of SO<sub>2</sub>. Then transfer this green solution to a 600 c.c. beaker containing about as much steel, free from chromium, as there is supposed to be iron in the ferro-chromium. For example, if the ferro is supposed to contain 60 per cent chromium, use 0.160 gram of steel. The steel is dissolved in 30 c.c. 1 : 3 sulphuric acid before the reduced chromium solution is added to it. Put this standardizing mixture through all of the analytical operations given for the actual analysis of the ferro-chromium, including the addition of the nitric acid.

#### CALCULATIONS.

The ferrous ammonium sulphate used by the 0.500 gram K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is, for example, 102.6 c.c. The percentage of chromium in the dichromate is 35.35. Therefore  $0.500 \times 35.35 \div 102.6 = 0.001724$ , or 1 c.c. of dichromate equals 0.001724 gram of chromium.

A check standardization using 0.600 gram of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> gave 1 c.c. equals 0.001713. The average value is 0.001718. Suppose 0.300 gram of a ferro-chromium required 99.9 c.c. of the sulphate standard:  $99.9 \times 0.001718 \div 0.3 = 0.5721$ , or 57.21 per cent chromium.

#### CARBON.

The total carbon can be obtained quickly by the means of some oxidizing flux in a stream of oxygen. Direct combustions with oxygen alone are very incomplete, at least with temperatures of 950° C. and under. Decarbonize 1 gram of 60-mesh sample with 4 grams of red lead, either in the gas or electrically heated furnaces. (See pages 203 to 245.)

#### ALUMINUM.\*

Proceed as in ferro-vanadium, page 18.

\* Read near the bottom of page 139.

**PHOSPHORUS AND SULPHUR.**

Fuse 2 grams, twice, with sodium carbonate and niter. Fuse each time with 20 grams of carbonate and 5 of niter. Add 5 c.c. of the aluminate. Precipitate the combined filtrates from the water solutions of the fusions with 1 : 1 HCl and proceed as in ferro-vanadium, getting the sulphur by completely acidulating the filtrate from the aluminum hydroxide, evaporating once to dryness, filtering and finishing by barium chloride in acid solution. Obtain blanks on fluxes and reagents and deduct the same from the barium sulphate found. A third fusion is often necessary to remove all chromium, phosphorus, aluminum and sulphur from the ferro-chrome.

*Second Method for Phosphorus and Aluminum.*

Fuse 2 grams of finely ground sample twice for five minutes with sodium peroxide in a nickel crucible. Dissolve in water, in a dish, as described under chrome ore. Filter after each fusion, washing with sodium peroxide water. For phosphorus the combined filtrates are treated with 5 c.c. of the sodium aluminate solution, and phosphorus and sulphur determinations are then proceeded with as in the sodium carbonate and niter fusion method: The aluminum hydroxide is precipitated by adding 1 : 1 hydrochloric acid until the former settles out well, still keeping the solution slightly alkaline to prevent interference of the chromium. The water solutions of the fusion should be boiled 10 seconds in porcelain or platinum vessels to remove the hydrogen peroxide before adding hydrochloric acid to precipitate the aluminum as hydroxide, hydrogen peroxide being a reducing agent in acid solution.

*For Aluminum.*

- (1) First add to the filtered, hot water solution of the peroxide fusions 1 : 1 hydrochloric acid, and note if any cloudiness or white precipitate forms before acidity is reached. If a precipitate appears, it is filtered out, washed and examined for alu-

minum, silicon and phosphorus as given under ferro-vanadium, page 19.

(2) To the filtrate from the aluminum add 5 c.c. of sodium aluminate and 5 grams of sodium carbonate. Precipitate the remainder of the phosphorus as aluminum phosphate, and proceed as already described for phosphorus and sulphur. Add the phosphorus obtained from the aluminum, if any is found in the ferro, to that obtained from the added aluminate, to get the total phosphorus.

(3) To avoid (2), 100 mgs. of metallic aluminum can be added to (1) to insure the presence of sufficient aluminum to carry out all of the phosphorus. The metal is added as chloride by dissolving it in 10 c.c. of 1 : 1 HCl. Deduct this 100 mgs. from the total aluminum found to get the aluminum in the test.

*Third Method for Phosphorus, Sulphur and Aluminum.*

(A) Fuse 1 gram of the finely ground sample with 10 grams of sodium carbonate and 2 grams of niter. Dissolve the fusion in water. Filter, wash with sodium carbonate water. Roast the residue at a low red heat until filter paper is gone. Dissolve the oxides in hydrochloric acid, and transfer the solution to a 1000 c.c. boiling flask. Make a peroxidation, adding 100 mgs. of metallic aluminum exactly as given under the second method for phosphorus in ferro-vanadium, page 24.

(B) The filtrate and washings from the water solution of the sodium carbonate and niter fusion are examined for phosphorus, sulphur and aluminum exactly as given under the first method for these elements.

For phosphorus the aluminum hydroxide precipitates obtained from the peroxidation (A) and from the filtrate from the sodium carbonate and niter fusions (B) are combined by putting the hydrochloric solutions of the aluminum hydroxide precipitates together before converting to nitrates. Finish as in the first method.

The object of this third method is to avoid all but one of the fusions required in the first method. Deduct blanks made on

all acids, sodium peroxide and fluxes used. (Either by sodium peroxide fusions or by sodium carbonate and niter fusions considerable yellow chromate color is obtained from the water solution of third fusions of ferro-chromium.)

#### SILICON.

Obtain the silicon as in high silicon ferro-vanadium; i.e., fuse if necessary, acidulate with hydrochloric acid, and evaporate twice to dryness.

#### MANGANESE.

Remove the chromium by zinc oxide, and proceed as in chrome steel soluble in sulphuric acid.

If fusions are required, separate the manganese by prolonged heating of the water solutions of the double fusions with alcohol as in high manganese ferro-vanadium. (Page 16.)

#### IRON.

The residue from the water solution of sodium carbonate and niter fusions is treated for iron as outlined for iron in ferro-vanadium. Or the precipitates remaining on filters after separating chromium, aluminum and phosphorus by the peroxide method can be roasted, dissolved in conc. hydrochloric acid, evaporated to fumes with sulphuric acid, reduced with zinc and titrated with permanganate solution for iron as in ferro-vanadium.

#### CHROMIUM IN CHROME ORE.

Fuse 0.6 gram with 8 grams of sodium peroxide in a 45 c.c. porcelain crucible. Keep the fusion molten for five minutes. Three or four melts can be made of chrome ore in a porcelain crucible before the peroxide cuts through.

Place the crucible in a 375 c.c. casserole. Cover with a watch glass. Stand the crucible in the bottom of the casserole. Allow water to flow slowly down the under side of the watch glass and drop into the open crucible. The melt promptly boils up and dissolves in a few moments. Remove the crucible. Boil the

water solution, without filtering, for one-half hour to remove all hydrogen peroxide. The excess of peroxide would reduce some of the chromic acid, if allowed to remain, just as soon as the fusion is acidulated with the sulphuric acid. Add 50 c.c. excess of 1 : 3 sulphuric acid.

Add 3 c.c. of the ferricyanide indicator to the cold sulphuric acid solution and titrate it as in ferro-chrome using the same standard. Standardize by fusing 0.340 gram of potassium dichromate in 8 grams of peroxide in a porcelain crucible, and complete the operation as in actual analysis. Multiply the number of milligrams of metallic chromium found by 152 and divide by 104 to obtain the milligrams of chromium oxide in the ore, or

$$\text{Cr} \times \frac{19}{13} = \text{Cr}_2\text{O}_3.$$

As the samples of ferro-chromium and chrome ore are likely to vary somewhat, especially in the case of ferro-chromium, several determinations should be made of the same sample and the results averaged.

Porcelain crucibles are not suitable for fusion of *metals* with sodium peroxide, as great heat is generated, causing the crucible to crack. This is not the case in chrome ore.

#### INSOLUBLE FERRO-CHROMIUM.

Ferro-chrome that is not attacked by acids can be conveniently assayed for chromium as given for chrome ore, but as the porcelain crucible usually cracks during the cooling a new crucible is needed for each fusion.\*

Weigh 0.500 † gram of the finely ground ferro and fuse it with 8 grams of sodium peroxide.

\* Iron crucibles are preferable for this work. Use a 65 c.c. crucible. Keeping the lid on, grasp the body of the crucible with the forceps; hold it in the flame of a Bunsen burner until molten. Then give the crucible a slight rotary motion for a period of 3 or 4 minutes, or until the entire mass is in a state of homogeneous fusion.

† From 0.2 to 0.25 gram if Cr in the ferro exceeds 50 per cent Cr.

**THE DETERMINATION OF CHROMIUM IN FERRO-CHROMIUM  
BY FUSION IN AN IRON CRUCIBLE.**

Fuse 0.200 gram of the ferro if the chromium is about 65 to 70 per cent in chromium content, or a proportionately larger weight if the chromium content is lower, in a 70 c.c. iron crucible with 8 grams of sodium peroxide. In making the fusion the crucible is held in a pair of tongs and given a moderate swirling motion in the flame of an ordinary Bunsen blast burner. In two minutes the melt should be liquid and after two more minutes the fusion should be perfect. During the fusing it is wise to place the burner in an enameled ware pan as, in case the flux cuts through the crucible, the drops of the red hot flux will be caught in the pan, instead of being spread far and wide. After cooling the crucible is placed in a 600 c.c. casserole; a lid is placed on the latter and the fusion is dissolved in 150 c.c. of water which is allowed to flow very slowly down under the watch glass into the open crucible. The water solution of the fusion is boiled for a half hour to remove all hydrogen peroxide; the crucible is removed from the casserole; 150 c.c. of 1 : 3 sulphuric acid are added; and the solution is heated for 10 minutes. The iron scales are filtered out on an asbestos plug (see page 8) and the plug is washed with water thoroughly; the filtrate and washings are diluted to 400 c.c. with distilled water; 3 c.c. of indicator are added (5 grams of potassium ferricyanide dissolved in 120 c.c. of water) and the solution is titrated to the first distinct blue with the same standard as given on page 141.

*Chrome Ore.* Chrome can also be analyzed as above for chromium, taking 0.500 gram for the analysis; but for the most accurate work the author prefers the method given on page 140, as the fusion in porcelain dissolves in the sulphuric in the most satisfying way, being as clear as a filtered solution except for a few scattering pure white flakes of floating silicic acid. The fusion in porcelain is also desirable for iron determination as the sulphuric acid solution can be reduced at once without

separating the chromium and titrated for iron with the standard permanganate solution (see page 48).

*Standardization.* For either of the above methods fuse 0.400 or 0.450 gram of recrystallized potassium dichromate in 8 grams of the sodium peroxide and put the same through all of the above operations and titrate the resulting solutions with the permanganate solution to be standardized, calculating the chromium value of the standard in the same manner as given on page 48.

*Aluminum.* To avoid all fusions in platinum for the determination of this element, ferro-chromium can be decomposed in the iron crucible as above, getting the *sulphuric* acid solution of the fusion which is then peroxidized as described on page 23, beginning at the point where one is directed to dilute to about 300 c.c. Make at least three peroxidations if the Al is 10 per cent, or over, using hydrochloric acid to *redisolve* the iron.

## CHAPTER VI.

### PART II.

#### THE ANALYSIS OF CHROME CEMENT.

*Ignition Loss.* Heat 1 gram of sample for a half hour in a weighed platinum crucible at a bright heat and weigh the crucible and its contents again and note the loss of weight. Return the crucible to the flame and heat at 10 minute intervals until the loss for 10 minutes heating no longer exceeds 0.0002 gram. The total loss of weight is calculated to percentage as the ignition loss.

*Silica, Iron and Aluminum Oxides.* Fuse 0.5 gram of sample with 15 grams of potassium acid sulphate ( $KHSO_4$ ) in large platinum crucible, in the manner described on page 51, until a clear solution is obtained. Cool; dissolve in water and hydrochloric acid. Boil; filter off the silica; wash it; finish it as usual getting the loss of weight with HfI and a few drops of conc.  $H_2SO_4$ . The residue remaining in the crucible after this evaporation and ignition is fused with 4 grams of  $KHSO_4$ . Dissolve it as in the main fusion, adding the solution to the main filtrate from the silica. This filtrate contains all of the iron and aluminum. The aluminum is separated from the iron by peroxidation with sodium peroxide until a filtrate is obtained that does not show any more precipitate with the HCl than a blank determination. (See page 23.) The iron on the filter from the last filtration together with any that may be adhering to the walls of the peroxidation flask is dissolved in HCl and finished by reduction with stannous chloride as in iron ore. The iron found is calculated to FeO. The aluminum is purified from occluded salts by redissolving it in HCl and reprecipitating it with a slight excess of ammonia. Before filtering off the aluminum it should be boiled for some minutes.

It is washed with ammonium nitrate wash, ignited, blasted, cooled and weighed as  $\text{Al}_2\text{O}_3$  plus a little silica which is removed by evaporation with some HFl plus 10 drops of conc.  $\text{H}_2\text{SO}_4$ . Deduct blanks.

*Chromic Oxide.* Fuse 0.3 or 0.4 gram of the sample in 8 grams of sodium peroxide in an iron crucible and finish as in chrome ore. (See page 140.)

#### RESULTS.

	Per cent.		Per cent.
Ignition loss.....	2.34	Silica.....	3.21
Iron monoxide ( $\text{FeO}$ )..	30.00	Chromic oxide ( $\text{Cr}_2\text{O}_3$ )..	40.80
Alumina.....	23.20		

Note. Sodium carbonate fusions are not successful as a method of decomposing the above cement.

## CHAPTER VII.

### ALUMINUM IN STEEL.

WEIGH 3 grams of chromium and tungsten steel or 6 grams of plain carbon steel into a half liter flask filled with carbon dioxide. Pour into the flask 10 c.c. 1 : 1 hydrochloric acid for every gram of steel. Warm until action ceases with CO<sub>2</sub> passing into the flask. Cool, and add a saturated solution of sodium carbonate (use a measured amount) until the iron precipitate dissolves rather slowly. Now add a slight excess of barium carbonate free from alumina. Add the carbonate in a thick paste. Fill the flask to the neck with water. Mix the contents thoroughly by repeatedly inverting the stoppered flask. Permit CO<sub>2</sub> to escape, occasionally, during the mixing. Allow the contents of the flask to settle twelve hours. Mix with pulp; filter and wash with water containing 5 gms. of NaCl per 500 c.c. 40 times to remove the greater portion of the ferrous iron.

Dissolve the residue on the filter, consisting of a mixture of tungsten, iron, aluminum and chromium compounds, with hot 1 : 1 hydrochloric acid. Wash the filter free of iron test. Ash this filter, after washing it free of acid, in a porcelain crucible. Transfer the ash to a platinum crucible and fuse it with 20 times its weight of Na<sub>2</sub>CO<sub>3</sub>. Dissolve the fusion in HCl and add it to the main solution of the precipitate obtained as above with the barium carbonate. Evaporate the filtrate and washings from the solution of the residue to 20 c.c. Cover the dish with a watch glass and add an excess of potassium chlorate. Heat with cover on until all spraying is over. Remove the cover and evaporate to dryness. Add 20 c.c. conc. hydrochloric acid. Cover and boil gently until all is in solution except a yellow residue of tungstic acid, which will appear if the steel contains tungsten. Add 50 c.c. of water. Boil twenty minutes. Filter. Wash with 1 : 20 hydrochloric acid until the filter no

longer gives an iron test. Evaporate again to dryness. Dissolve, filter and wash as before. Precipitate the filtrate and washings with a slight excess of ammonia in a casserole. Boil a few minutes. Add paper pulp; use ashless pulp. Filter. Wash with ammonium nitrate water until free from chloride test. Use the same number of filters on all tests and on the blank test. The latter is made at the same time as the regular analysis. Roast off the paper in a large platinum crucible, and fuse the ash with 10 grams of sodium carbonate and 2 grams of niter, keeping it molten for a half hour. Leach out with water, filter, wash, add 1 : 1 hydrochloric acid to this fusion, 1 c.c. at a time, until the aluminum separates out in a white flocculent precipitate if present in considerable quantity, or until the solution looks milky if the percentage is small. Be sure to keep the solution at all times distinctly alkaline, or much vanadium and chromium, if any be present, will be carried out with the aluminum. Proceed further as in ferro-vanadium. (See aluminum in ferro-vanadium, page 18.)

The aluminum gives only a faint cloudiness to the solution if present in small quantity. In the latter case wait two hours before filtering.

Fuse the iron residue a second time. Dissolve melt in water. Filter; wash; precipitate with acid. If much precipitate of aluminum hydroxide, etc., is obtained from the second fusion, then fuse a third time and proceed as before. Combine all three precipitates of aluminum hydroxide and finish as given under aluminum in ferro-vanadium, page 18.

Run a blank including all chemicals and filter paper pulp; deduct the aluminum so obtained from the final weight of  $\text{Al}_2\text{O}_3$ .

#### *Second Method.*

Proceed as in the first method until the hydroxide precipitates have been obtained with ammonia. (After the chlorate treatment; the subsequent evaporation to dryness; and removal of any tungsten that may be present.) Roast the paper from the hydroxide precipitates. Dissolve in hydrochloric

acid and transfer this solution to a 1000 c.c. boiling flask, and then finish by wet sodium peroxide separation as given under the second method for aluminum in ferro-vanadium, page 23. Deduct blanks. Remove phosphorus and silicon. Multiply the pure  $\text{Al}_2\text{O}_3$  by 53.033 and divide by the weight taken for analysis to obtain per cent of aluminum.

The separation of aluminum from iron by sodium peroxide has some advantages. If the operator thinks he has carried the addition of the HCl too far, he can redissolve the hydroxide right in the solution by adding a slight excess of the peroxide. Then the precipitation can be repeated with more caution after the usual 20 seconds boiling to remove the excess of  $\text{H}_2\text{O}_2$ .

While it is not essential, it is easier to precipitate aluminum hydroxide free from vanadium and chromium if some sodium carbonate is present. The carbon dioxide causes the aluminum hydroxide to precipitate while the solution in which the precipitation occurs is still alkaline. For this reason 10 grams of sodium carbonate are added to all solutions from which aluminum is to be precipitated by HCl unless the carbonate is already present.

#### *Small Amounts of Aluminum, Uranium, Vanadium and Chromium.*

Less than 0.05 per cent of aluminum, uranium or vanadium can be separated from the bulk of the iron in 50 grams of the sample by the method given on page 146. The residue on the filter after the barium carbonate precipitation consists of all of the U, Cr, V and Al in the sample together with the excess of barium carbonate and some iron. Wash the residue with sodium chloride water about twenty times. (1) This residue can be analyzed for Al as given on page 146. (2) It can be ashed, fused with a little peroxide, the fusion dissolved in HCl, converted to nitrates and finished for Cr and V as in steel. (3) For uranium the ashed residue can be analyzed as in carnotite ore as given on page 289.

In this way minute percentages of the above elements can be determined with extreme accuracy. Also minute amounts of titanium can be separated from the bulk of the iron in the same way.

## CHAPTER VIII.

### PART I.

#### COPPER IN STEEL AND PIG IRON.

DISSOLVE 15 grams of drillings in 300 c.c. of 1.20 nitric acid in an 800 c.c. beaker. Heat until all action ceases. Add an excess of KMnO<sub>4</sub> solution of the same strength as used for phosphorus in steels. Boil gently for 30 minutes. If the KMnO<sub>4</sub> disappears during the boiling, add more of it. Steels require from 4 to 8 c.c. and pig iron from 25 to 30 c.c. of the permanganate solution.

In pig iron add 5 c.c. of hydrofluoric acid before boiling with permanganate of potash. Heat 10 minutes. Then boil with the KMnO<sub>4</sub> solution.

After boiling the pig iron or steel with permanganate solution, add enough wet pulp to nearly fill a 50 c.c. graduated cylinder. Filter through double 12 cm. filters into an 800 c.c. beaker. Wash the pulp, etc., free from iron with a dilute nitric acid wash consisting of 5 c.c. of 1.20 nitric acid diluted with 200 c.c. of water. This takes about 40 washings.\*

To pig iron or steel containing from 0.010 to 0.030 per cent of copper, add at this stage 20 c.c. of a solution of potassium ferricyanide, made by dissolving 5 grams of the crystals in 120 c.c. of distilled water. Stir thoroughly and permit the solutions to stand.

If the copper content is unusually high, add 2 c.c. of the ferricyanide solution for every milligram of copper supposed to be present in the steel. If nickel is present, it is precipitated with the copper, but forms more slowly.

As there is a tendency to form blue cyanide of iron the filtra-

\* Read near the top of page 152 concerning the addition of ammonia to prevent excessive formation of iron cyanide.

tions should be proceeded with in about a half hour. Add as much paper pulp as in the first filtrations, filter and wash five or ten times with water containing 5 c.c. of ferricyanide solution per 100 c.c. of distilled water. Use a 15 cm. filter.

Roast off the pulp in a porcelain crucible. Dissolve the iron, nickel and copper oxides with 5 c.c. of conc. hydrochloric acid. Rinse the solution into a 200 c.c. beaker. Dilute to 150 c.c. with water and pass H<sub>2</sub>S for a half hour at a rapid rate. This removes the copper from nickel and any iron that may have been precipitated as cyanide.

Filter on a small filter; wash twenty times with H<sub>2</sub>S water. Burn the paper in a 45 c.c. porcelain crucible. Dissolve the oxide in 20 c.c. 1.20 nitric acid, warming until all black residue is dissolved except perhaps an occasional flake of carbon from the filter paper. Rinse the solution into a 5 ounce beaker, keeping the volume as low as possible for copper of 0.020 per cent and under, in order that the blue color with ammonia may be distinct. Copper as low as 0.015 per cent gives a distinct blue if properly manipulated. Now add a saturated solution of sodium carbonate, a little at a time, until a precipitate forms. Then add 0.5 c.c. of conc. ammonia. Titration follows with a standard solution of potassium cyanide, made by dissolving 2.244 grams of potassium cyanide and 5 grams of stick potassium hydroxide in water and diluting to 1000 c.c. 1 c.c. of this standard should equal about 0.00064 to 0.00069 gram of metallic copper. Standardize the solution by adding 10 and 15 mgs. of metallic copper of 99.8 per cent Cu to 15 grams of any steel or pig iron. Weigh out also two 15 gram portions of this same steel or iron, but add no copper to them. Put all four weights through the entire operation, titrating each one to the disappearance of the blue as given under "Titration."

*Titration.* Place a 5 ounce beaker containing distilled water beside the one containing the copper to be tested. Add the cyanide standard to the test until it is as free from even a slight blue tint as the beaker of distilled water.

This method has been tested with known amounts of copper

added to steels, and with steels standardized by the old standard methods. It is much more rapid, and results check very satisfactorily. Filtrations might be hastened by using pulp filters on porcelain plates and applying slight suction.

### CALCULATIONS.

#### *Pig Iron Sample.*

- (1) 16.0 second reading of burette.  
7.9 first reading of burette.  
 $\underline{8.1}$  equals c.c. of standard used.  
No copper added.
- (2)                  48.0  
15 mgs. copper added  $\underline{16.2}$   
 $\underline{31.8}$  equals c.c. of standard used.
- (3) 10 mgs. copper added 23.6  
 $\underline{\quad\quad\quad 0.0}$   
 $\underline{23.6}$  equals c.c. of standard used.
- (4) 31.8 - 8.1 equals c.c. of standard used by 15 mgs. Cu.
- (5) 23.6 - 8.1 equals c.c. of standard used by 10 mgs. Cu.
- (6) From (4) we have  $15 \div 23.7 = 0.632$ , or 1 c.c. of cyanide equals 0.000632 gram Cu. ( $0.998 \times 15 \div 23.7$ )
- (7) From (5) we have  $10 \div 15.5 = 0.643$ , or 1 c.c. of cyanide equals 0.000643 grams Cu. ( $0.998 \times 10 \div 15.5$ )
- (8) From (1) we have  $8.1 \times 0.00064 \div 15 \times 100 = 0.0345$ , or 0.0345 per cent copper in the sample of pig iron, 15 grams having been taken for analysis.

### QUALITATIVE VALUE.

With 2 grams of sample as little as 0.1 per cent of copper gives a very noticeable yellowish cloud when the potassium ferricyanide is added to a solution of steel treated as described. Hence the method affords a rapid qualitative test for the presence of copper in sufficient quantity to be injurious (0.05 per cent and over) for *most* purposes for which fine tool steel is used. The operator can easily decide whether the precipitate is copper or nickel. If it is copper, the precipitation is almost instantaneous. If it is nickel, the reaction is noticeably slower and the precipitate is of a brown color, closely resembling that of iron hydroxide. A yellowish cloud, forming, at once, on the addition of the first c.c. of the precipitant, is characteristic of copper. If

this be followed by a more slowly forming brown precipitate,\* then both elements are present. Many makers of tool steel insist that the copper content of best tool steel be under 0.02 per cent. Several steels doing fine work, however, have been analyzed by the author and found to contain copper greatly in excess of this limit. It is largely a question of what sort of a tool is to be made from the steel.

The tendency to form blue ferricyanides of iron on adding potassium ferricyanide to ferric solutions, the author has found, can be eliminated sufficiently to prevent serious clogging of filters, by keeping the iron solution somewhat neutral, after *first boiling it with an excess* of permanganate solution and filtering out the excess of manganese oxide. After removing the latter by filtration, add 1 : 1 ammonia until the hydroxide of iron dissolves rather slowly.† Then add the ferricyanide and proceed as already described.

As the copper ferricyanide precipitates almost instantly, forming a very considerable cloud of yellowish precipitate even with 0.03 per cent copper, it is very finely divided, and has a tendency to run through the filter. The first portion that is filtered should be poured back on the paper until it runs through clear. Then proceed with the filtration. Stand the main filtrate aside when washing begins, and, should the latter be cloudy, filter with a little pulp on a small filter and add it to the main precipitate.‡

When precipitating a large quantity § of copper by this method — for example, sixty or one hundred milligrams — the

\* Add at least 20 c.c. of the ferricyanide when testing for nickel.

† Do not carry the neutralization too far as in nearly neutral solutions the nickel and copper precipitate very slowly with the ferricyanide.

‡ Pay no attention to any clouding of the filtrate that may occur after the latter has stood for some time.

§ The foregoing method is especially useful for very small per cents of Cu and Ni, i.e., 0.100 down to 0.005 per cent, as from 15 to 20 grams of sample can be taken. For higher per cents it is easier to weigh out from 1 to 3 grams of plain carbon steel; dissolve in 1 : 1 HCl and pass H<sub>2</sub>S at once. Then finish as in the ferricyanide method from the point where H<sub>2</sub>S was passed through the solution of the copper and iron oxides.

The ferricyanide method is the best for high speed steels. See page 156, the bottom paragraph. Read also page 154 in this connection.

nearly neutral solution should be largely diluted, making the volume from about 800 c.c. before adding the precipitant. (See Separation of Copper and Nickel from Vanadium by Ferricyanide of Potassium.) It is better to precipitate such large amounts of copper with H<sub>2</sub>S.

#### SMALL AMOUNTS OF COPPER AND NICKEL IN STEEL AND IRON.

When analyzing steel, iron, etc., for copper, do not carry the neutralization, given in the top paragraph of page 152, too far, as in nearly neutral solutions, small amounts of nickel ferricyanide precipitate very slowly, and the precipitation of the copper ferricyanide is also delayed.

The method described for copper on pages 149 to 152 is designed for small amounts of copper, that is, for percentages ranging from 0.100 to 0.001 and for equally low per cents of nickel. If nickel in such small per cents is asked for, get the ferricyanide precipitates of the nickel and copper together in the same way as directed on pages 154 to 156 using 15 grams of sample and the same method of solution as given for copper in steel, pages 149 to 151, separating the nickel from the copper and determining it as given on pages 154 to 156.

#### LARGE AMOUNTS OF COPPER IN PLAIN AND ALLOY STEELS.

If the percentage of copper exceeds 0.100 per cent, then dissolve but 1 or 2 grams of the sample, and proceed as described. If the sample is an alloy steel, then it is necessary to decompose the same in the manner given for chromium on page 8, whether the amount of copper be large or small. If the amount is small then 15 grams should be taken for the analysis and a proportionate amount of sulphuric acid followed by an equal amount of the 1.20 nitric acid, that is, 200 c.c. of the 1 : 3 sulphuric acid; and after the action of this acid is over, aided by heating for a half hour, then 200 c.c. of the 1.20 nitric acid are added and the analysis is finished as for copper in plain carbon steel.

## CHAPTER VIII.

### PART II.

#### SEPARATION OF NICKEL AND COPPER FROM IRON AND VANADIUM BY POTASSIUM FERRICYANIDE.

PROCEED as outlined for copper in steel, except smaller weights of sample are usually required.

For nickel and copper in ferro-vanadium dissolve 1 or 2 grams of sample, using 30 c.c. of 1.20 nitric acid for each gram. If the ferro is high in silicon, carbon and aluminum, and for this reason only partly soluble in nitric acid, add a few c.c. of hydrofluoric acid to the solution after action with nitric acid is over. Heat until all metallic or gritty particles are in solution. Or the insoluble part can be broken up by a sodium carbonate and niter fusion; dissolved in hydrochloric acid; the latter removed by evaporation to fumes with sulphuric acid; the sulphate dissolved in water and returned to the main solution. Then boil the latter with an excess of permanganate solution; filter out the manganese oxide as described under Copper in Steel. To the filtrate and washings 1 : 1 ammonia is added until a slight precipitate of hydroxide is obtained that dissolves slowly. The copper and nickel are precipitated with potassium ferricyanide as in Copper in Steel. Large amounts of nickel — i.e., from 0.025 to 0.050 gram — precipitate quickly, but smaller quantities should be permitted to settle for one hour before filtering. It is best to let all nickel tests stand at least one hour. Add as much paper pulp from ashless filters as will nearly fill a 15 cm. filter. The precipitate and pulp are filtered out; washed a few times; dried; ignited in a large porcelain crucible; the ash transferred to a 6 ounce beaker; dissolved in 30 c.c. of aqua regia. Clean the crucibles with 10 c.c. of the latter and add the cleanings to the main part. (Nickel oxide dissolves with

some difficulty, requiring considerable heating.) 50 c.c. 1 : 3 sulphuric acid are added to the solution; evaporated to 12 c.c.; diluted to 300 c.c.; the copper is precipitated with H<sub>2</sub>S; filtered out and washed thoroughly with H<sub>2</sub>S water and finished as in steels. The filtrates and washings from the H<sub>2</sub>S precipitation will contain all of the nickel and a little iron. Evaporate this filtrate and washings to 50 c.c., and add 30 c.c. of conc. nitric acid to oxidize the iron and destroy any remnant of the H<sub>2</sub>S. Heat with a cover on the dish until all action is over. Then remove the cover, cool, add 30 c.c. 1 : 3 sulphuric acid and evaporate until slight fumes of sulphuric anhydride are obtained. Cool; add 50 c.c. of water; and filter into a 600 c.c. beaker. Add 10 grams of citric acid; make faintly ammoniacal; cool and titrate the nickel with potassium cyanide. (See the author's modified cyanide method for Nickel in Steel, page 164.)

If it is desired to determine a very small quantity of nickel in steel, about 0.3 per cent and under, weigh 10 or 15 grams of sample and proceed as outlined, getting the nickel and the copper from the one analysis. If the nickel content is likely to be under 0.1 per cent, it is convenient to use 10 grams of sample. If it is in excess of 0.2 per cent, it is best to use 5 grams. The precipitate requires that considerable paper pulp be mixed with it to secure rapid filtrations. Wash the pulp, etc., 5 times with water containing a drop of sulphuric acid and 5 c.c. of the ferricyanide solution per 100 c.c. of water. As the precipitate has a tendency, at times, to run through the filter when first poured on it, this first portion of the filtrate is refiltered until it is clear. When filtering large precipitates, such as would be obtained from 50 mgs. of nickel, it is expedient to use 2 funnels to hasten matters. Nickel up to 50 mgs. from a 5 gram weight of sample, or 10 mgs. of nickel from 10 grams of sample, can be conveniently precipitated from a volume of 500 c.c. For large amounts of nickel in steel, — i.e., 0.50 per cent and over, — the foregoing method is not nearly so rapid as the one described on pages 164 to 175, but for minute quantities, or where it is necessary to first remove the bulk of the iron or the vanadium (much

vanadium in solution gives ammoniacal citrates of an almost greenish black color,\* greatly interfering in the method just referred to), it is a useful preliminary to the cyanide titration. There would seem to be no reason why the ferricyanide could not be applied, with suitable modifications, to the determination of copper and nickel in ferro-manganese, chrome and other ferros and metals that are not precipitated by this useful reagent (notably aluminum) in acid solution. Manganese is precipitated by the ferricyanide in neutral or slightly ammoniacal solution as quickly as are copper, nickel and zinc in slightly acid solution. (See the author's volumetric method for all percentages of manganese above 2 per cent, page 193.)

By the above process the copper and nickel can be determined, quantitatively, in the same analysis with the chromium and the vanadium when the copper does not greatly exceed 0.25 per cent: Two grams are taken for the analysis. The nickel and copper ferricyanides are filtered out after the regular titrations have been made for V and Cr. Of course no time must be lost in making the vanadium part of the titration, as copper soon clouds the solution after the addition of the ferricyanide. The author uses this scheme to get Cr, V, Ni and Cu from the one analysis. In such cases the titrated solution is allowed to stand a half hour before filtering. If brown nickel ferricyanide begins to appear, 40 or more c.c. of potassium ferricyanide are added and filtration is delayed for an hour.

\* Read page 174.

## CHAPTER VIII.

### PART III.

#### COPPER IN METALLIC COPPER — VOLUMETRIC.

THE author regards the following cyanide titration as a simple and rapid method for the assay of metallic copper. Scarcely any element interferes that cannot be removed by precipitation with  $H_2S$  in hydrochloric acid solution. If carried out with proper attention to details, there is no more accurate volumetric method in commercial use. It is essential that the potassium cyanide be standardized with metallic copper of known copper content, or by some recrystallized c.p. salt of copper. The metal is preferable, and is put through every analytical detail that is applied to the analysis of the test.

Operate with 0.5 gram of the test and of the standard copper drillings, running both standardizations and tests parallel with each other. Use copper of 99.8 per cent purity for standardizing. The drillings are dissolved in 10 c.c. 1.20 nitric acid, evaporated to 5 c.c., filtered from any tin, etc.; the filter washed with water containing a little nitric acid. The filtrate and washings are evaporated to fumes with 20 c.c. 1 : 3 sulphuric acid. The copper sulphate is dissolved in water. Any lead is removed by filtration and washed with water containing a little sulphuric acid. Hydrogen sulphide is then passed through the filtrate, in a volume of 400 c.c., with 5 c.c. excess of 1 : 1 hydrochloric acid for every 100 c.c. of water, until the copper has completely separated in hot solution. Filter. Wash with  $H_2S$  water. Return filter and all to the beaker. Add 50 c.c. of 1.20 nitric acid. Give standardizations and test the same excess of acid. Warm with a cover on until copper sulphide is dissolved. Filter out pulp. Wash thoroughly with water containing a little 1.20 nitric acid. Ignite the pulp; dissolve the residue in

1.20 nitric acid; add the solution to the filtrate and washings; evaporate to 20 c.c. Add 1.5 grams of citric acid and a slight excess of sodium carbonate. Use a saturated, filtered solution of the carbonate and add it until effervescence ceases entirely. Titrate the clear blue solution with a standard of potassium cyanide made by dissolving 22.434 grams of the best cyanide together with 5 grams of potassium hydroxide in distilled water and diluting to 1 liter. One c.c. of this standard usually equals about 0.00635 gram of copper; but this value should always be fixed by the operator himself, in the manner just outlined. The following modification removes uncertainty as to the end point when titrating large amounts of copper. Add the potassium cyanide as usual until the blue color is almost gone. Follow with additions of a cyanide standard of one-fifth strength until all blue tint has disappeared.\* Then add 2 c.c. of a 20 per cent solution of potassium iodide in water; then silver nitrate standard until a slight cloud of silver iodide is formed as in Nickel in Steel. (Chapter IX.) Now add about 10 c.c. excess of this dilute cyanide standard. Again add the silver nitrate standard until a slight millessness is produced in the solution; 2.925 grams of silver nitrate are dissolved in water and diluted to 500 c.c. for this work.

#### STANDARDIZATION.

Suppose 0.500 gram of copper drillings of 99.8 per cent purity were taken, and that after putting this metal through all of the foregoing analytical operations the following data were obtained:

First, The concentrated cyanide standard required to *nearly* discharge the blue color equals 76.9 c.c.

Second, The one-fifth cyanide standard required to *entirely* discharge the blue equals 26.8.

Third, The silver nitrate solution needed to produce a slight

\* Now wait for 30 minutes to one hour to give the KCN and the copper time to completely react together before adding the KI and silver nitrate to get the excess of KCN. This should be done because the blue color of the copper disappears long before the copper and the KCN have entirely ceased to combine.

milkiness in the solution, after the blue color was entirely gone, equals 13.6 c.c.

Fourth, 8.3 c.c. of silver nitrate were used to produce a cloudiness, again, after the addition of 11.3 c.c. of the one-fifth cyanide standard in excess, or 1 c.c. of  $\text{AgNO}_3 = 11.3 \div 8.3$ , or 1.36 c.c. of the one-fifth cyanide standard.

Fifth, Therefore  $26.8 - (13.6 \times 1.36) = 8.3$ , or the amount of one-fifth cyanide used in reaction with the copper, or 1.66 c.c. of conc. cyanide to be added to 76.9, or a total of 78.56 c.c. of conc. KCN required to combine with the 0.500 gram of 99.8 per cent pure copper. Hence 1 c.c. of the concentrated cyanide standard equals  $0.499 \div 78.56 = 0.00635$ , or 1 c.c. = 0.00635 gram of copper.\*

Mr. R. M. Clarke of this laboratory suggested that it might be an advantage to use silver nitrate to obtain a more exact end point instead of relying on the disappearance of the blue. The analytical details are the author's.

#### *Further Details.*

(a)

Stir the copper sulphide into small particles before heating it with the 1.20 nitric acid, or an insoluble black lump may form. Then heat very gently at first. Keep the temperature considerably below 100° C. at all times to prevent occlusion of some of the copper sulphide by the liberated sulphur, and the formation of a black insoluble residue. Pay no attention to any milkiness that may appear when the nitric acid solution of the pulp ash is added to the nitric solution of the main sulphide.

(b)

The titration can be accurately accomplished, omitting the one-fifth cyanide standard: Add the concentrated standard until the blue is entirely gone.† Then add the KI indicator and follow with the silver nitrate until a very slight permanent

\* The author now uses  $\frac{1}{2}$  this strength, or 1 c.c. equals 0.003175 gram of copper. A 100 c.c. burette, graduated to  $\frac{1}{10}$ th c.c., is the best adapted to this method.

† Then pause for at least 30 minutes before adding the KI.

cloudiness occurs. Next drop into the beaker an excess of 5 c.c. of the conc. cyanide. Again add the silver nitrate until a very faint milkiness is once more apparent that does not disappear after 15 seconds stirring.

(c)

Further, it is quite important to add the cyanide, while discharging the blue color, very slowly when the latter begins to fade: Add the standard three drops at a time; then stir vigorously for 20 seconds. If the blue is not all gone, add three drops more and stir again for a period of twenty seconds. By proceeding in this way and making the titrations in small volumes — beginning with a volume of not over 100 c.c. — the disappearance of the blue affords an accurate end point but more experience and judgment is required than when using the cyanide and "silver" scheme. After thus carefully removing the blue tint proceed to determine the actual cyanide used by means of titration (b).

*Calculations.*

(1) 0.500 gram of copper required 84.2 c.c. of the concentrated cyanide to just discharge the blue.

(2) 24.8 c.c. of the  $\text{AgNO}_3$  standard were required to produce the *first* faint cloudiness.

(3) 21.9 c.c. of  $\text{AgNO}_3$  were needed to produce the second faint cloud after the addition of 5 c.c. excess of the conc. KCN. Therefore  $21.9 \div 5 = 4.38$ , or 1 c.c. of the cyanide equals 4.38 c.c. of the silver nitrate standard.

(4) From (2) and (3) we have  $24.8 \div 4.38 = 5.66$ , or the excess of the cyanide standard in the solution. From (1)  $84.2 - 5.66 = 78.54$ , or the number of c.c. of the cyanide required to combine with the 0.500 gram of copper. There is always an excess of the cyanide when the blue color is gone, but the reaction between the copper and the KCN is not usually completed for at least 30 minutes after the disappearance of the blue.

## TITRATION OF COPPER IN THE PRESENCE OF OTHER METALS.

If the solution contains 3 grams of citric acid and a moderate excess of the sodium carbonate, 0.500 gram of copper can be accurately titrated in the presence of 0.100 gram of zinc, or iron, or 0.050 gram of lead: The citric acid is added to the nitric solution of the metals; then the carbonate until effervescence ceases, and 5 c.c. in excess. The volume before titration should be about 100 c.c. When much iron is present the alkaline solution is a dark green. The cyanide standard is added until the green is gone and the clear amber color of the citrate of iron appears. Then determine the excess of the cyanide as usual.

As much as 0.100 gram of arsenic can be present without having the slightest effect.

The author made entirely successful titrations of 0.500 gram of copper dissolving with it 0.200 gram of antimony; also in the presence of 0.100 gram of cadmium. The end point given by the disappearance of bluish tints from the white antimony oxides and cadmium carbonate was noted. This end point was obtained as in (c). The precipitates were then removed by filtration through double filters, and the excess of cyanide was determined in the filtrate and washings in the usual way with silver nitrate. The precipitates had to be poured through the filters several times to secure clear filtrates. The precipitates were washed ten times with dilute sodium carbonate water.

When titrating copper in the presence of 0.200 gram of bismuth the disappearance of the blue was taken as the end point, as the basic bismuth clouded the solution. With but 0.100 gram of bismuth in solution the entire titration, as outlined in (b), was successfully carried through before the solution was perceptibly clouded.

Large quantities of manganese interfere with the titration of copper only in so far as dark colored solutions are formed when the cyanide is added, thereby obscuring somewhat the end point between the cyanide and the "silver nitrate." More citric

acid is required. Add to the standardization about as much manganese as there is likely to be in the copper that is to be assayed. Use at least 6 grams of citric acid per 0.200 gram of Mn.

#### PRECIPITATION BY ALUMINUM.

When using this well-known method one can proceed as at first described until the filtrate and washings from the lead sulphate are obtained. Evaporate the former to 20 c.c.; add 10 c.c. 1 : 3 sulphuric acid and a piece of aluminum  $1\frac{1}{2}$  inch square by  $\frac{1}{16}$  inch thick. Heat nearly to boiling for 30 minutes, or until the solution is colorless. Remove the aluminum and decant the solution through a 9 cm. filter; wash the filter 15 times with water containing a few drops of 1 : 3  $H_2SO_4$ . Return the filter to the 150 c.c. beaker in which the precipitation was made.

The filtrate and washings from the metallic copper should be tested with  $H_2S$  and, if a brown coloration is obtained, continue to pass the gas until the small precipitate of copper collects. Filter it out; wash it with  $H_2S$  water containing a drop or two of 1 : 3  $H_2SO_4$ . Put this filter in the same beaker with the metal; add 20 c.c. 1.20 nitric acid; heat below boiling until the copper is dissolved; filter off the pulp; wash it 40 times with water containing a little 1.20 nitric acid; evaporate the filtrate and washings to 20 c.c. in a 600 c.c. beaker and titrate the copper with cyanide and "silver nitrate." *Hold the copper solution about one hour after discharging the blue with cyanide and before titrating with the cyanide and silver nitrate.*

The author found that owing to the slowness of the reaction between the KCN standard and the copper ammonium compound that the above precaution of holding the solution for an hour after discharging the blue of the copper, and then, after the said interval, determining the excess of cyanide in the manner given on page 159, (b) and (c), is an essential one. It gives such satisfactory results that he prefers this volumetric method to all others for the determination of copper. As the chem-

ist usually has several titrations of copper to make, at the same time, no delay of any consequence results, as a number of tests can be given the first part of the titration for the discharge of the blue color, and, by the time the blue has been discharged from the last test, the first one has been standing the required time. It can then be at once finished with the cyanide and silver nitrate. The author now uses and recommends one-half the strength of cyanide standard given on page 159, that is, 1 c.c. equals 0.003175 gram of copper.

## CHAPTER IX.

### PART I.

#### \* THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON AND MANGANESE.

IN applying the method of T. Moore † to the determination of nickel in steel, the directions given on page 183, Analysis of Steel Works Materials by Brearley and Ibbotson, were followed: One gram of steel was dissolved in a 150 c.c. beaker with 10 c.c. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased 10 c.c. of nitric acid (1.20) were added, and the contents of the beaker were boiled to about one-half. 16 c.c. of dilute sulphuric acid were poured into the solution and also 3 grams of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 c.c. beaker, and rendered faintly but distinctly ammoniacal.

The nickel was titrated with a standard solution of potassium cyanide, using a measured amount of standard silver nitrate and 2 c.c. of a 20 per cent solution of potassium iodide as an

*Note:* For Brunck's Dimethylglyoxime Method for Nickel and the author's modification of this separation, see page 175.

indicator. The deep red color of the citrate of iron greatly obscures the end point. The authors complain of this color and recommend the use of a condensing lens to cast a beam of light through the darkness. In the presence of chromium the writer

\* [Reprinted from the *Journal of the American Chemical Society* (with additions), Vol. XXIX, No. 8, August, 1907.]

† *Chemical News*, 72, 92.

found that a still more somber gloom settled down over the close of the reaction. The authors mentioned also state that this element retards the union of the cyanide and the nickel, causing the recurrence of the cloud of silver iodide.

After struggling with the process for some time and always carefully separating the chromium, and with it the iron, in chrome steels, an attempt was made to dispel the darkness and also to avoid these tedious separations: Less citric acid per gram of steel was taken, and the dark red shaded to blackness.

Naturally, the amount of citric acid per gram of steel was then increased, that is, 6 grams of citric acid per gram of steel were used, and a marked improvement was noted. Still more citric acid caused a complete lifting of the shadows.

The following modified procedure was finally adopted for nickel steels after having been thoroughly tested with plain carbon steels to which known amounts of nickel had been added: Dissolve 1 gram of steel drillings in a 150 c.c. beaker with 20 c.c. of hydrochloric acid (1 : 1). When action ceases add 10 c.c. of nitric acid (1.20).

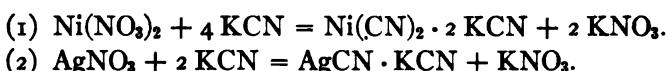
Reduce the volume of the solution to about 15 c.c., keeping the beaker covered during the boiling. Remove the beaker from the fire and pour into it 8 c.c. of conc. sulphuric acid diluted with 24 c.c. of water. The presence of the sulphuric acid is essential to a sharp end reaction between the cyanide standard and the silver iodide in the subsequent titration.

Transfer the contents of the beaker to one of 600 c.c. capacity containing *twelve* grams of powdered citric acid. Stir until the citric acid is dissolved. Render this solution *faintly* but *distinctly* alkaline with ammonia, using one part of concentrated ammonia diluted with one part of water. A large excess of ammonia causes low results. Stand the beaker in running water until it is cold. The volume of the solution should now be about 300 c.c. Much larger volumes than 300 c.c. should be avoided, as great dilution retards the end point, causing the cloud of silver iodide to disappear and then to reappear again in a few minutes.

The faintly ammoniacal condition \* can be easily controlled by adding the ammonia rather slowly and noting the changes of color that ensue: The first change is to amber, then to yellowish green, then to distinct green, then to a light shade of green, then to a yellow almost matching the yellow color of the acid solution. The reappearance of the yellow tint indicates that alkalinity is nearly attained.

A little more ammonia now causes a brownish shade, which is evidence that the ammonia is in slight excess. The moderately alkaline citrate of iron obtained in the proportion of 1 gram of iron to 12 grams of the citric acid yields a bright greenish yellow solution in plain nickel steels instead of being of a dense dark red shade.

To the cold solution two c.c. of a 20 per cent solution of potassium iodide are added. From a 50 c.c. burette a standard solution of silver nitrate is dropped into the same beaker, producing with the iodide a white turbidity. The standard potassium cyanide is added with constant stirring until the cloud of silver iodide just disappears, which it does on being converted into silver cyanide. Nickel cyanide is first formed, and then the silver cyanide is produced:



If the directions are followed as given, the titration can be accomplished at almost the full speed of the burette. If the titrated solutions are permitted to remain in the open beakers for a time, a film usually appears on the surface of the liquid. No account is taken of it, as its presence is most likely due to a superficial loss of ammonia. The reactions are always found to be completed when the body of the solution is freed of the iodide precipitate.

\* One can, also, use litmus paper; add ammonia, drop by drop, until 1 drop of 1:1 ammonia just turns the red litmus blue, then add 10 drops excess of the ammonia and no more. A person with the average sense of smell can add ammonia until a slight sweet smell is obtained and then the 10 drops of excess with better success than with the use of litmus.

*Standards.* From the equations as given, 5.85 grams of silver nitrate are equivalent to 4.4868 grams of potassium cyanide. This weight of cyanide dissolved in 1 liter of water gives a value of 1 c.c. equals about 0.001014 gram of nickel.

As comparatively little silver nitrate is needed with each analysis, it is not advisable to prepare more than a half liter of the water solution of this salt, using 2.925 grams per 500 c.c. of distilled water.

The potassium cyanide standard should contain about 5 grams of potassium hydroxide to the liter, which renders it quite permanent. The solutions are readily standardized by applying them to a plain steel to which a known amount of nickel has been added. The chemically pure double sulphate of nickel and ammonium is a convenient standardizing medium. For example, 0.2 gram and 0.25 gram of the double sulphate can be weighed into 150 c.c. beakers together with 1 gram of plain carbon steel drillings.

This mixture is then put through all of the foregoing manipulations and titrated with the cyanide solution that is to be standardized. The number of c.c. of the silver nitrate and of the potassium cyanide solution used in this titration are noted. An excess of 10 c.c. of the cyanide is now added and in turn titrated with the silver nitrate solution until a distinct cloud of silver iodide is produced. This second titration gives the relation between the silver solution and the cyanide.

An actual case will illustrate the calculations: In sample No. 3477, 1.7 c.c. of standard silver nitrate solution were required to produce a distinct turbidity and also to combine with any excess of potassium cyanide standard. In all, 35 c.c. of the cyanide were consumed in the titration. When the cloud of silver iodide had just been dispelled, an excess of 9.8 c.c. of cyanide was allowed to flow into the clear solution. Just 10.1 c.c. of silver nitrate standard were needed to produce a reappearance of the cloudiness. Therefore  $9.8 \div 10.1 = 0.97$ , or 0.97 c.c. of cyanide standard solution equals 1 c.c. of silver nitrate. Hence instead of deducting 1.7 c.c. from 35 c.c.,

$1.7 \times 0.97$  or  $1.65$  c.c. were deducted, leaving  $33.35$  c.c. of cyanide combined with the nickel in this steel.

To a plain carbon steel  $0.200$  gram of double sulphate of nickel and ammonium were added put through all of the steps of a regular analysis. This mixture required  $28.75$  c.c. of cyanide. The nickel salt contains  $14.86$  per cent of nickel, or  $0.200 \times 0.1486 = 0.02972$  gram of nickel were present. Hence  $0.02972 \div 28.75 = 0.00103$ , or  $1$  c.c. of standard cyanide solution is equivalent to  $0.00103$  gram of nickel. No. 3477, as has been stated, required  $33.35$  c.c. of the cyanide standard, and therefore contains  $0.00103 \times 33.35 = 0.03435$ , or  $0.03435$  gram of nickel, or  $3.435$  per cent.

*Chromium-nickel Steels.* When chromium is present proceed exactly as in plain nickel steels except that twenty-four grams of citric acid per gram of steel are used. This proportion of citric acid is adequate to render the end point quite as easy to see as in ordinary nickel steels. The action is prompt and free from recurrence of turbidity. Of course, cloudiness through the entire solution will occur, as the ammonia is dissipated from it, after it has stood for some time in an open beaker.

The tabulation (1) that follows furnishes satisfactory proof that chromium does not interfere with the successful technical estimation of nickel in its presence:

TABLE I.

Sample.	No Chromium Added. Nickel Found, Per Cent.	Per Cent of Chro- mium Added to a Portion of the Same Steels.	Nickel Found after the Addition of Varying Amounts of Chromium.
Number.			
525	5.09	4	5.10
2991	4.44	2	4.45
7239	3.24	1	3.28
3017	4.96	1	5.03
612	3.47	0.5	3.47
7273	3.29	1	3.31
622	3.56	0.5	3.56
7288	3.32	2	3.41
7289	3.11	2	3.16
663	3.57	6	3.59
2991	4.44	3	4.47

The chromium was introduced in the form of recrystallized chemically pure potassium dichromate. The dichromate crystals were mixed with a weighed amount of nickel steel drillings before the addition of the 20 c.c. of hydrochloric acid. The combined action of the nascent hydrogen from the steel, the excess of boiling hydrochloric acid and the ferrous chloride reduced the chromate to chromic chloride, thus duplicating the conditions found when a chromium-nickel is similarly treated.

Determination by this modification of the cyanide method can be finished in from 45 to 50 minutes, either in the presence or absence of any per cent of chromium likely to be met with in steels or alloys soluble in the acids given. In this laboratory *duplicate* determinations in nickel or nickel-chromium steels are made in the time just specified. By the process one can decide in a few minutes whether or not nickel is present in a given steel and just how much. Tungsten, if present, does not interfere, appreciably, as has been noted by the authors mentioned in this article. The writer had two different amounts of nickel added to a steel containing several per cent of chromium and from 16 to 17 per cent of tungsten. This steel was then carried through exactly as though no tungsten or chromium were present, using the method as given for chromium-nickel steels.

Nickel Added, Gram.	Nickel Found.
0.0297	0.0299
0.03715	0.0372
None	0.0006

Table 2 demonstrates that neither vanadium, tungsten, chromium, nor molybdenum, when present in the amounts given, interferes appreciably in technical analysis. These amounts represent extreme cases, especially for the vanadium, it being equivalent in one instance to 3.5 per cent V when one gram of steel is taken.

Tests were then made in the same manner in the presence of molybdenum and vanadium as follows:

TABLE 2.

Name.	Kind of Steel or Mixture.	Nickel Added, Gram.	Nickel Found, Gram.
J. R. Steel.....	Contains 10% ± Mo.....	0.0297	0.0295
Do.....	....do.....	0.0222	0.0223
Do.....	....do.....	None	0.0002
Bxx-173 steel.....	Contains 4% Mo and 4% Cr.....	0.0223	0.0222
Do.....	....do.....	0.0297	0.0296
Do.....	....do.....	None	0.0004
A mixture.....	0.920 gram of steel.....	0.0297	0.0298
.....	0.030 gram of nickel.....	.....	.....
.....	0.018 gram of vanadium.....	.....	.....
A mixture.....	0.840 gram of steel.....	0.0223	0.0227
.....	0.022 gram of nickel.....	.....	.....
.....	0.035 gram of vanadium.....	.....	.....
A blank.....	1.000 gram of steel.....	None	0.0008
.....	0.035 gram of vanadium.....	.....	.....

As copper also forms cyanides, its presence would cause results to be too high, but copper is avoided in good steel making. Its presence is unlikely in greater amounts than 0.06 per cent, although the writer, on one occasion, found as much as 0.25 per cent in a low carbon steel, not a *crucible* steel, however. Crucible steel rarely contains over 0.04 per cent copper. The choice brands are under 0.03 per cent in copper.

Wishing to test the extent to which nickel could be titrated in the presence of large percentages of chromium, iron being also present, the mixtures as given in Table 3 were titrated with potassium cyanide. The various salts were weighed into 150 c.c. beakers, together with the proper amounts of steel drillings. The same proportions of hydrochloric, nitric, citric and sulphuric acids were employed as are herein given for nickel-chromium-steels, and were applied in the same manner.

A sufficient quantity of the salts of chromium and nickel, and of the steel drillings, were taken to give a total of one-half gram of metals in the mixture.

## DETERMINATION OF NICKEL IN PRESENCE OF CHROMIUM 171

Double sulphate of nickel and ammonium ( $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ ), potassium dichromate and steel drillings free from nickel were used as sources of nickel, chromium and iron, respectively.

To obtain the nickel value of the cyanide standard under conditions similar to those existing in the mixtures tested, standardizing mixtures of these salts were prepared varying from the mixtures tested as much as 1 per cent to 20 per cent in the different constituents.

For mixtures exceeding 10 per cent of nickel a standard cyanide solution with a nickel value of 1 c.c. = 0.0031 gram of nickel was used. The standardizing mixtures were dissolved and treated exactly as the mixtures tested. The same method of standardization was observed in the work recorded in Table 4.

TABLE 3.

Per Cent of Metals.			Gram of Nickel.	
Ni.	Cr.	Fe.	Added.	Found.
30	40	30	0.1499	0.1494; 0.1495
60	20	20	0.2999	0.3003; 0.2989
20	40	40	0.1029	0.1022
5	90	5	0.0250	0.0248; 0.0244
4	92	4	0.0200	0.0199
1.5	95	3.5	0.00749	0.00805; 0.00822
0.5	99	0.5	0.00249	{ 0.00225; 0.00243 0.00247; 0.0026
0	98.9	1.0	None	None

Table 3 demonstrates that nickel may be estimated by the foregoing modified cyanide process, using the proportions of citric acid as given, with sufficient accuracy for works analysis, and indeed for most practical purposes, even when the percentage of chromium is as much as 99 per cent, and the nickel content is but one-half of one per cent.

\* The titration of the mixtures given in Table 3, and containing the larger amounts of chromium, requires considerable

\* Read the determination of nickel in the presence of much chromium, page 174.

practice on the part of the operator. The work should always be carried out in duplicate. The disappearance of the cloudiness in the presence of 0.100 to 0.450 gram of chromium in a volume of 350 to 400 c.c. is much more exactly observed when the mixture containing the iodide cloud is compared, from time to time, with a *similar* mixture which is perfectly free of this milky turbidity. The dilution of the deep purple, or wine color, of these ammoniacal mixtures of citrates to more than 300 to 400 c.c. renders the end point but slightly more distinct, and has the great objection of retarding the reaction between the cyanide and the nickel. The increase above 24 grams of citric acid, in the solution, even to the extent of adding 60 grams of citric acid, did not relieve the density of color to any perceptible extent.

When titrating with a standard, 1 c.c. of cyanide = 0.0031 gram of nickel (three times the strength used for steels), do not also increase the strength of the silver standard to equal it, but still retain the silver nitrate standard as given for steels. A silver nitrate solution sufficiently concentrated to be equivalent, volume for volume, to the cyanide standard (1 c.c. = 0.0031 gram of nickel) on being dropped into the solution containing the potassium iodide, does not produce the usual opalescence, alone, but forms curds of iodide that do not readily combine with the cyanide standard. The end point is reached and the main body of the solution is free of cloud while curds of silver iodide still lie on the bottom of the beaker. The weaker silver nitrate standard, or 5.85 grams of silver nitrate to the liter, produces with the potassium iodide a finely divided cloud of precipitate that combines promptly with the strong cyanide standard, giving a sharp end point. Weigh, therefore, 2.925 grams of silver nitrate, diluting to 500 c.c., and 13.4604 grams of the best grade of potassium cyanide, diluting to 1000 c.c., for titrations of solutions containing from 0.100 to 0.300 gram of nickel; 1 c.c. of this silver nitrate solution should be equivalent to  $\frac{1}{3}$  c.c. of the concentrated cyanide standard (1 c.c. cyanide = 0.0031  $\pm$  grams of nickel).

The titration of nickel by potassium cyanide in mixtures containing large percentages of manganese with varying amounts of chromium and iron was also tried.

As in the experiments outlined in Table 3, mixtures were prepared to contain one-half gram of metallic substances. The same nickel and chromium salts were employed. Potassium permanganate crystals supplied the manganese.

The crystals of double sulphate of nickel and ammonium, potassium dichromate and potassium permanganate were weighed into a 150 c.c. beaker with the steel drillings. To this were added 20 c.c. of dilute hydrochloric acid. The contents of the beaker were then boiled, after the first action was completed, until the chromate and permanganate were reduced. An addition of 10 c.c. of nitric acid (1.20) followed, and the analysis was carried out exactly as given for chromium-nickel steels, using 24 grams of citric acid. The results obtained are given in Table 4. Sulphuric acid was added as in the process for steels.

TABLE 4.

Per cent of Metals.				Gram of Nickel.	
Ni.	Mn.	Cr.	Fe.	Added.	Found.
41	20	10	30	0.2059	0.2058
20.6	40	20	20	0.1029	0.10228
15	60	15	10	0.0750	0.0752
1.5	95.5	1	2	0.00749	0.00762
0.25	94.9	2	2.9	0.00124	0.00122
.....	94.9	2	4	None	0.00006

Table 4 gives evidence of the fact that nickel can be accurately determined in the presence of large percentages of chromium and manganese, if the conditions herein given are carefully observed. In the hands of a practiced operator no difficulty was experienced in the analysis when as much as 95 per cent of manganese was in solution with but 0.25 per cent of nickel.

Where large amounts of reduced chromium are encountered

with nickel, the latter can be titrated to a better advantage by boiling the sulphuric acid solution of the sample with an excess of  $\text{KMnO}_4$ ; filtering out the manganese oxide and then proceeding with the addition of the citric acid, etc. (see E. D. Campbell and W. Arthur, J. Am. Chem. Soc., 30, 1116-20, July, 1908). There is not the slightest need for all this extra work for any amount of chromium ever found in steels, unless it is desired to determine this element in the same analysis with the nickel. In that event use 4 grams of steel and proceed as in CrV steels (Chapter II); and, when the solution is ready for the titrations, *divide it in two equal portions*. Finish one portion for Cr and V by the method in Chapter II. Finish ONE-HALF of the other part for nickel, adding citric acid, etc. This procedure avoids the reoxidizing and refiltering resorted to by Messrs. Campbell and Arthur; and also any necessity of making the objectionable spot tests. It affords an easy way of getting Cr, V and Ni from the one analysis.

*Add the citric acid after neutralizing the free acid when large amounts of chromium or vanadium are present with the nickel.*

By first performing the neutralization before adding the citric acid, the latter is prevented from reducing the vanadium or chromium and, in this way, the intense dark colors are eliminated. It is still better to not only neutralize the free acid of the chromic acid-nickel or the vanadic acid-nickel solution, but to also convert the citric acid to ammonium citrate before adding this organic compound to the almost or entirely neutral solution of the nickel and chrome, or nickel and vanadium. This of course applies only to the filtrate after boiling with permanganate to oxidize the vanadium to the vanadic and the chromium to the chromic state. This oxidation is highly to be recommended when large amounts of vanadium or chromium are present.

After adding the ammonium citrate, the usual amount of excess of ammonia is introduced and the citrate will gradually dissolve the iron hydroxide after prolonged stirring.

**THE COMPLETE ANALYSIS OF "30 PER CENT" NICKEL STEEL.**

*Iron.* Dissolve 0.3 or 0.45 gram of sample in 30 c.c. of 1.20 nitric acid in a porcelain dish, and when the action is over, evaporate the solution to dryness; ignite the bottom of the dish to a dull red to destroy the carbon; cool; dissolve in 20 c.c. of conc. HCl and finish as in iron ore by reduction with stannous chloride and titration with potassium dichromate standard. The nickel does not interfere except to turn the spot tests cloudy, but not so quickly but that the end point can be seen. 0.45 gram of sample required 53.2 c.c. of the standard; 53.2 times 0.00565 divided by 0.45 times 100 equals 66.7 per cent iron.

**STANDARDIZATION IN THE PRESENCE OF NICKEL.**

Dissolve 0.300 gram of the U. S. Bureau Sibley iron ore together with 1.00 gram of double sulphate of nickel and ammonia, as above, and put it through all of the operations as given. Titrate it with the regular dichromate standard as used for iron ore (9.8 grams of recrystallized  $K_2Cr_2O_7$  dissolved in water and diluted to 2000 c.c.). This gives a factor of 1 c.c. equals 0.00565 gram of iron, that is, 36.7 c.c. of the standard were used, hence 0.300 times 0.692 divided by 36.7 equals 0.00565.

The carbon, manganese, etc., were determined as in plain steels.

**RESULTS.**

	Per cent.		Per cent.
Carbon.....	0.20	Silicon.....	0.125
Manganese.....	0.74	Nickel.....	32.27
Phosphorus.....	0.025	Iron.....	66.75
Sulphur.....	0.025		

**BRUNCK'S METHOD FOR NICKEL IN STEEL.**

This method is supposed to separate nickel from iron, chromium, zinc, manganese and cobalt. The presence of a large quantity of manganese requires the precipitation to be made from acetic solution. The procedure for steel is to dissolve from

0.5 to 0.6 gram in 10 c.c. of 1 : 1 HCl with heat. Oxidize with nitric acid; boil off the red fumes; silicon is not removed; it would seem to the writer that it would be safer in some steels to remove the silicon by evaporation to dryness.

Add from 2 to 3 grams of citric acid and make the solution slightly ammoniacal to see if any precipitation occurs. If the solution remains clear, add HCl drop by drop until slight acidity is attained. Heat to near boiling; add 20 c.c. of a 1 per cent solution of dimethylglyoxim in alcohol. Now drop in ammonia to slight alkalinity. Let stand for one hour and filter hot. Wash with water. The red precipitate is caught on a Gooch or Munroe crucible and, after being thoroughly washed, is dried for 45 minutes at from 110 to 120° C. The weight obtained is multiplied by 0.20326 to convert it to metallic nickel which is then calculated to percentage.

The percentage of 20.326 corresponds to the formula of  $C_3H_{14}N_4O_4Ni$ . Prettner recommended the holding of the solution for an hour before filtering off the scarlet precipitate. Those wishing to read the original descriptions of the method should consult Zeitschrift für Angew. Chemie, 1907, Nr. 47, S. 1844. Dr. O. Brunck. Also Chem. Ztg., 33, 1909, p. 396.

#### A MODIFICATION OF BRUNCK'S METHOD BY SOLUTION OF THE RED PRECIPITATE IN NITRIC ACID AND TITRATION OF THE SOLUTION IN THE USUAL WAY WITH KCN AND SILVER NITRATE.

Proceed as for nickel as in Brunck's method, obtaining the red precipitate which is washed 15 times with 500 c.c. of water containing 10 c.c. of a 2 per cent solution of the dimethyl. The precipitate is dissolved off the filter with 25 c.c. of 1.20 nitric acid, allowing the solution to run into the beaker in which the precipitation of the nickel was made. Wash the filter about 30 times with water containing 10 c.c. of 1.20 nitric acid per 500 c.c. of water, or until the wash water no longer gives a test for nickel with the dimethyl. Add 15 c.c. of 1 : 3 sulphuric acid

to the nitric acid solution of the red precipitate; boil 20 minutes; cool; add 5 grams of citric acid; make faintly ammoniacal; add 10 drops of 1 : 1 ammonia and finish for nickel by titration with KCN and silver nitrate. By this method the U. S. nickel-chrome standard No. 32 (1.62 per cent Ni) gave 1.63 per cent nickel, and the U. S. nickel standard No. 33 (3.33 per cent Ni) gave 3.36 per cent Ni.

One should be able to use this method for the determination of small amounts of nickel by taking large weights of the sample. Elements like manganese, vanadium and chromium, that give very dense dark citrates when in the "ous" state, could be analyzed for small per cents of nickel in the above manner by separating away the bulk of these elements from the nickel. (See the Determination of Small Amounts of Nickel in the Presence of Large Amounts of Cobalt, page 314.) The idea of making such a modification of Brunck's method was suggested to the author by Mr. A. G. Greenameyer. The above details are the writer's.

For the Determination of Nickel by Electrolysis, see page 316.

## CHAPTER IX.

### PART II.

#### THE ANALYSIS OF NICKEL-CHROMIUM ALLOY.

THE widespread application of true nickel-chromium and nickel-chromium-iron alloys to resistance heating has made further work for the analyst.

The author has analyzed several varieties of these useful alloys as follows:

##### NICKEL.

Dissolve 0.5 gram of the wire in a No. 5 porcelain dish with a mixture of 20 c.c. conc. HCl and the same amount of conc.  $\text{HNO}_3$  and evaporate to 15 c.c. Add 100 c.c. of conc.  $\text{HNO}_3$  and evaporate to 20 c.c. Transfer the solution to a 600 c.c. beaker; add 40 c.c. of 1 : 3  $\text{H}_2\text{SO}_4$ ; dilute to 200 c.c.; heat to boiling; add permanganate of potassium to the boiling solution until an excess of brown manganese oxide remains without perceptible change after a half hour of boiling; cool; filter on an asbestos plug or through an alundum thimble, making sure that none of the manganese oxide runs through, as the filtrate must be perfectly clear. Cool; add 1 : 1 ammonia until a precipitate starts to form; add 15 grams of citric acid made slightly alkaline to litmus paper by ammonia. Add 10 drops more of the ammonia, if necessary to render the solution slightly alkaline. Titrate the solution with the concentrated KCN standard given on page 172. To standardize the cyanide under conditions similar to the alloy, put the following mixtures through all of the above operations and then titrate them with the KCN: Mixture No. 1, 1 gram of the nickel-ammonium-sulphate, and 200 mgs. of potassium dichromate; mixture No. 2, 2 grams of nickel-ammo-

nium sulphate and 200 gms. of the dichromate. The nickel-ammonium sulphate used in this work was checked by electrolysis and found to contain 14.6 per cent nickel, hence mixture No. 1 contained  $0.146 \times 1.00$  or 0.146 gram of nickel, and mixture No. 2 contained  $0.146 \times 2.00$  or 0.292 gram of nickel.

#### CHROMIUM.

Dissolve 0.500 gram of the finely ground sample exactly as given for nickel and proceed with the analysis as for nickel and filter off the excess of manganese oxide as in the case of the nickel. Cool the filtrate if the titration is to be finished forthwith; omit the neutralization with ammonia; and titrate, after adding 40 c.c. of 1 : 3 sulphuric acid and diluting further to 250 c.c. with water. Titrate with the same strength of sulphate and permanganate standards as are given on pages 33 and 34. Do not use any ferricyanide indicator as the nickel would be precipitated and hide the end point. First add the sulphate standard until all red tints are gone and there remains only the chrome green; then add an apparent excess of about 10 c.c. Next titrate with the equivalent permanganate standard until a faint permanent pink flush is visible through the green of the chromium. The amount of the sulphate used less the number of c.c. of the permanganate required to produce the pink end point is multiplied by the value of the double sulphate in chromium per c.c. The result equals the number of milligrams of chromium in the 0.500 gram of sample. The standardization is accomplished by putting the following known mixture through all of the foregoing operations: 0.250 gram of plain carbon steel, 0.100 gram of recrystallized potassium dichromate and 2 grams of nickel-ammonium sulphate; also the same amounts of steel and nickel salt with 0.200 gram of the dichromate. These mixtures are titrated in the same way as described for the sample itself and the value of the sulphate in chromium is calculated in the usual way. The value of the dichromate in metallic chromium is taken as 35.35 per cent Cr.

#### MANGANESE.

Dissolve 0.300 gram of the wire in a mixture of 10 c.c. of conc. nitric acid and 5 c.c. of conc. hydrochloric acid. Evaporate to 5.0 c.c.; add 50 c.c. of conc. nitric acid and evaporate to 10 c.c.; add 25 c.c. more of the nitric acid and again evaporate to 10 c.c. Transfer to a 10 X 1 inch tube and finish as in chrome steels, as directed on page 15.

#### CARBON.

Twist several strands of the wire into a rope and take millings therefrom as described under Milling (see page 221). Then burn with red lead as in ferro-chromium.

#### SULPHUR AND SILICON.

The sulphur is determined as in the gravimetric method for alloy steels. The silicon is obtained from the insoluble matter filtered out before precipitating the sulphur with barium chloride.

#### IRON AND ALUMINUM.

Dissolve 1 gram of millings in a mixture of 20 c.c. of conc. HCl and 20 c.c. of conc.  $\text{HNO}_3$ . Heat until all action is over; boil down to 20 c.c.; transfer to a liter boiling flask; dilute to 300 c.c. and peroxidize, as described on page 23, getting filtrates A and B, and if B has a distinct yellow color, then a third peroxidation should be made, obtaining a third filtrate and washings C that are free from an appreciable yellow color, showing that all of the chromium has been separated from the iron present. The aluminum is obtained from A, B and C as in ferro-vanadium that is by adding 1 : 1 HCl slowly with *constant* stirring until turmeric paper is no longer *immediately* turned to even a suggestion of a brownish red color on being dipped into the solution. The operator can easily tell when he is approaching the end point by the sudden increase of the effervescence, as the acid is added;

also if aluminum is present to the extent of even one per cent the solution will have become cloudy and if several per cents are present, the usual white, flocculent, precipitate of aluminum hydroxide will have formed. Continue to add the acid until the turmeric shows no more immediate change of color than if it had been dipped into water. Of course in a minute or two the paper will take on a faint brownish red. At this stage the solution will change litmus paper at once to a distinct blue. A, B and C can be combined in one before performing the precipitation of the aluminum, or if the volumes are too great they can be treated separately and the precipitates combined on the one filter. The alkaline solution is brought just to a boil, before adding the acid, but in no case should the strongly alkaline solution be heated further, as by so doing large amounts of glass are dissolved. The precipitate of aluminum is then washed and dissolved off the filter, reprecipitated with a slight excess of ammonia and weighed as  $\text{Al}_2\text{O}_3$  plus a little  $\text{P}_2\text{O}_5$  and  $\text{SiO}_2$  and finished from that point on as given on page 19 and on page 20.

*The Iron:* All of the iron will be on the filter from filtrate C except a slight film which will be clinging to the walls of the boiling flask. The latter is cleaned by warming in the flask a little 1 : 1 HCl and the iron on the filter is dissolved off with hot acid of the same kind. The iron from the flask and the filter are combined and titrated as in iron ore after reduction with stannous chloride. To standardize the dichromate the following known mixture was put through all of the foregoing operations: 250 mgs. of standard iron ore, 0.100 gram of potassium dichromate and 2.00 gram of the nickel-ammonium sulphate. Also for a check, 0.260 gram of the iron ore, and the same amounts of the other two salts as before. The Sibley ore No. 27 of the U. S. Bureau of Standards is extremely useful as a known source of iron to add to all such standardizing mixtures. The salts of nickel and chromium are of course added only to have the standardizing mixtures as near the samples as possible.

## SOME TYPES OF NICKEL-CHROMIUM AND NICKEL-CHROMIUM-IRON ALLOYS.

	No. 1.	No. 2.	No. 3.	No. 4.
Carbon.....	0.12	0.35	0.30	0.14
Manganese.....	0.82	2.74	1.50	Trace
Sulphur.....	0.012	0.074	.....	0.027
Nickel.....	76.93	60.35	66.42	83.91
Chromium.....	16.40	10.12	19.37	13.97
Silicon.....	0.23	0.40	.....	.....
Iron.....	1.81	25.11	10.23	1.47
Aluminum.....	2.68	0.53	.....	.....

## CHAPTER IX.

### PART III.

#### THE ANALYSIS OF NICKEL-COPPER IRON ALLOY (MONEL METAL).

##### SILICON AND COPPER.

DISSOLVE 0.5 or 0.6 gram of the drillings or millings in a No. 5 porcelain dish with 35 c.c. of 1.20 nitric acid. In the same manner dissolve 2 standardizing mixtures as follows: (1) 0.100 gram of 99.9 per cent metallic copper and 2.00 grams of the double sulphate of nickel and ammonia. (2) 0.200 gram of the copper and 3.00 grams of the double sulphate. Heat until all action with the nitric acid has ceased; add 70 c.c. of 1 : 3 sulphuric acid and evaporate to thick white fumes. Add 100 c.c. of water; heat until all is in solution except a little white insoluble residue of flotant silicic acid which is filtered through a double 11 c.c. ashless filter and washed free of iron with water containing 10 per cent by volume of 1 : 3 sulphuric acid. Finish the washing with water; get the silicon from the residue on the filter as in steels, page 286, by loss of weight after evaporation with a few drops of conc. sulphuric acid and 10 c.c. of hydrofluoric acid. Any residue of oxides remaining after this evaporation and ignition is dissolved out with a little conc. HCl and the solution is added to the main filtrate from the silicon. This filtrate is diluted to 400 c.c. with water, heated nearly to boiling, and hydrogen sulphide is passed through it until the copper separates out well. Filter the sulphide of copper through a double 12½ cm. filter and wash with H<sub>2</sub>S water containing 5 drops of 1 : 3 sulphuric acid per 500 c.c. of water, giving not less than 40 washings. Dry the filter, burn it off at a low red heat in a porcelain crucible, and dissolve the copper oxide in

20 c.c. of 1.20 nitric acid. Transfer the solution to a 400 c.c. beaker; add 1.5 grams of citric acid; make neutral with a saturated solution of sodium carbonate and add 25 c.c. excess of the carbonate. Titrate the copper by the cyanide method as described on pages 157 to 163. For the indicator use a 20 per cent KI solution (20 grams of the KI to 100 c.c. of water); for the cyanide use 4.4868 grams to the liter; and for the silver nitrate dissolve 2.925 grams in water and dilute to 1 liter. It may be well to give the routine of the titrations here. Add the KCN to the solutions containing the various amounts of test and the known mixtures until all blue color is gone; then wait at least a half hour before proceeding with the cyanide and silver titration. Unless this pause is made discordant results will be obtained owing to the slowness of the complete reaction between the cyanide added to discharge the blue, and the copper. After the half to one hour interval, add 2 c.c. of the KI indicator, and then the silver nitrate until a slight white cloud of silver iodide appears that is permanent. To get the relation between the silver and the cyanide next add 5 c.c. of the KCN standard and again add the silver until the slight cloud again appears.

#### STANDARDIZATION AND CALCULATIONS.

Mixture No. 1 required 83.2 c.c. of the KCN to discharge the blue color, and after waiting for at least a half hour it required 6.5 c.c. of the  $\text{AgNO}_3$  standard to produce a slight cloud of silver iodide in the solution; further, on adding an excess of the KCN of 5 c.c. it required 4.3 c.c. of the  $\text{AgNO}_3$  to again produce a slight permanent cloud in No. 1. By this last titration, therefore, 4.3 c.c. of the "silver" equal 5.0 c.c. of the cyanide. Since 6.5 c.c. of the silver solution were needed to produce the first slight cloud after the 30 minute delay, then  $6.5 \times 5$  divided by 4.3 or 7.5 c.c. must be deducted from the 83.2 c.c. required to discharge the first blue in order to obtain the actual amount of the KCN standard that was used by the copper taken. This gives 75.7 c.c. of the KCN equal to  $0.100 \times 99.9$  of metallic copper or 0.0999 gram, or 1 c.c. of the KCN equals 0.00132

gram of copper. In the same way from mixture No. 2 it was found that 149.8 c.c. of the KCN equal 0.1998 gram of copper, or 1 c.c. of the KCN equals 0.001333 gram of copper. The average of the two standardizations was 0.00133. In the same manner 0.5 and 0.6 gram of the monel gave 26.6 and 26.9 per cent copper.

#### NICKEL IN MONEL.

The filtrates from the  $H_2S$  precipitation of the copper are evaporated to fumes with 100 c.c. of 1 : 3  $H_2SO_4$ ; cool; add 50 c.c. of water; and then 10 c.c. of conc.  $HNO_3$ ; heat to destroy any remaining hydrogen sulphide; filter if not clear, and titrate with cyanide and silver. For the cyanide standard dissolve 44.868 grams of KCN in water and dilute to 2 liters, and for the silver nitrate and the potassium iodide use the same strength as given for the copper. In making the titration add 2 c.c. of the KI and then the  $AgNO_3$  until a distinct white cloud of the silver iodide is formed; then add the KCN until the cloud just disappears; then add 10 c.c. excess of the KCN and just bring back the white cloud to get the relation between the silver nitrate and the KCN. As No. 1 (see copper) contained 2 grams of the nickel ammonium sulphate, there were present, theoretically,  $0.1486 \times 2.00$ , or 0.2972 gram of nickel. By the excess titration it was found that 1 c.c. of the  $AgNO_3$  equals 0.21 c.c. of the KCN. The first cloud produced by the addition of the 2 c.c. of KI did not disappear until 61.0 c.c. of the KCN had been added. In this standardization 2.4 c.c. of the  $AgNO_3$  were actually added to produce the cloud with the KI; and by the titration of the 10 c.c. of excess KCN, 47.6 c.c. of the  $AgNO_3$  were required to again reproduce the cloud; therefore, 61.0 c.c. less  $2.4 \times 10$  divided by 47.6, or less 0.504 c.c., equal 60.5 c.c. which equal 0.2972 gram of nickel, or 1 c.c. of the KCN equals 0.00491 gram of nickel. In the same way mixture No. 2 gave 1 c.c. of the KCN standard equals 0.00493 gram of nickel. From the 0.5 and 0.6 gram of the monel, 68.82 and 68.63 per cent nickel were found.

## IRON.

Dissolve 1 or  $1\frac{1}{2}$  gram of sample in 25 c.c. of 1.20 c.c. nitric acid in an 800 c.c. beaker and dilute to 500 c.c. Precipitate the iron with a considerable excess of ammonia and let the solution stand until the iron is well separated. Filter it off; wash the precipitate with 1 : 20 ammonia until the washings are no longer colored blue; then redissolve the iron with 40 c.c. of 1 : 1 HCl; wash the filter free of iron with 1 : 20 HCl and precipitate the filtrate and washings as before with an excess of ammonia; filter off the iron hydroxide; wash it as above; dissolve it as before; dilute the filtrate and washings from this HCl solution to 300 c.c.; heat to boiling; add stannous chloride until the iron is decolorized and three or four drops in excess; cool; add 35 c.c. of the mercuric chloride solution; stir and titrate at once with a dichromate of potassium made by dissolving 1.225 grams of this salt in water and diluting it to 1 liter. Add the dichromate standard until the solution being titrated no longer gives a blue spot test with potassium ferricyanide when two drops of it are mixed with the same amount of the ferricyanide indicator on the usual porcelain plate. To standardize the dichromate put enough of the iron ore furnished by the Bureau of Standards or of some other equally reliable iron standard through all of the foregoing manipulations as though Ni and Cu were present, and titrate with the dichromate standard. In one such analysis, enough iron ore standard was taken to equal 30 and 60 mgs. of metallic iron in solution. This gave 1 c.c. of the dichromate equals 0.00141 gram of iron.

*The mercuric chloride solution* is made by dissolving 50 grams of the salt in 1000 c.c. of water.

*The stannous chloride* is made by dissolving 10 grams of stannous chloride or an equivalent amount of pure tin in 100 c.c. 1 : 1 HCl.

*The ferricyanide* is prepared by dissolving 0.50 gram of this salt in 100 c.c. of water at the time it is to be used to get the sharpest end point.

## CARBON, MANGANESE, SULPHUR AND PHOSPHORUS.

The sulphur is found by the gravimetric method as in plain steels, as given on page 274, the carbon by direct combustion in oxygen, the manganese by the volumetric method given on page 276 and the phosphorus as given on pages 257 to 264.

## SOME ANALYSES OF MONEL METAL.

	No. 1.	No. 2.	No. 3.
Carbon.....	0.15	0.10	0.30
Manganese.....	.....	Trace	3.27
Phosphorus.....	0.020	0.017	0.045
Sulphur.....	0.043	0.020	0.063
Silicon.....	0.236	0.190	0.67
Iron.....	2.90	.....	3.98
Nickel.....	68.82	69.18	66.78
Copper.....	26.95	27.24	24.86

## CHAPTER X.

### PART I.

#### **FERRO-MANGANESE.**

##### **GRAVIMETRIC METHOD.**

DISSOLVE one gram of sample in 50 c.c. of 1.20 nitric acid in a No. 4 porcelain dish. Remove the watch glass. Evaporate to dryness. Ignite to low red heat to destroy the carbon. Replace the cover. Dissolve in 40 c.c. conc. hydrochloric acid. Heat until fumes of chlorine have disappeared. Filter into an 800 c.c. beaker. Wash the residue on the filter with 1 : 10 hydrochloric acid until it is free from iron test. Wash it further with water until it is free from chlorine test. Ignite the residue in a weighed crucible and finish for silicon as in steels.

Dilute the filtrate and washings to 300 c.c. Add dilute ammonia until one drop produces a precipitate that fails to dissolve with persistent stirring. Now add one drop, only, of 1 : 1 hydrochloric acid. Also pour into the solution 1.5 c.c. of ammonium acetate for every 100 mgs. of metallic iron supposed to be present. (The ammonium acetate solution is prepared by dissolving 50 grams of the salt in 50 c.c. of water. Add dilute ammonia to this solution a drop at a time until it smells very faintly of ammonia.\* Add water until the total volume of the acetate solution is 100 c.c.) Heat to boiling. Boil one minute. Permit the precipitate to settle a few moments. Stir in some paper pulp. Filter hot. Wash fifteen times with hot water containing 2 c.c. of ammonium acetate to 100 c.c. of water.

Redissolve the precipitate with 10 c.c. of hot 1 : 1 hydrochloric acid. Wash the filter free from iron test. Dilute the filtrate and washings to 200 c.c. and precipitate it again as before.

\* Or reacts slightly blue with red litmus paper.

Wash the precipitate. Combine this filtrate and washings with the original filtrate and washings. Evaporate all (after adding to the combined filtrates 5 c.c. of 1 : 1 hydrochloric acid) to 200 c.c. Filter if necessary. Add 25 c.c. of ammonium acetate solution. Heat to boiling in a platinum or porcelain dish. Add\* to the *boiling solution* 75 c.c. of a saturated solution of microcosmic salt, stirring continuously: Add a slight excess of ammonia, and continue to heat the precipitate and supernatant fluid with frequent stirring until the pink manganese phosphate changes from a flocculent slimy precipitate to a pink crystalline heavy one that settles rapidly to the bottom of the vessel. When cold, filter out the manganese phosphate and wash it with cold water until no milkiness is obtained from the washings on being acidulated with a drop or two of nitric acid and tested with a drop of silver nitrate solution.

Add 10 c.c. more of the precipitant to the filtrate and washings. If a precipitate forms after several hours, collect it; wash it as in the main precipitate. Dry the two filters containing the phosphate. Remove the latter to a large watch glass. Cover it. Burn its filter in a weighed platinum crucible at a low red heat until all black is gone. Now add the small residue, if any, obtained from the filtrate and washings tested with 10 c.c. of the phosphate of sodium and ammonium. When this residue has been burned white at the lowest possible heat, add the main phosphate precipitate and ignite it very slowly to prevent loss by dusting due to liberation of ammonia. Then raise the heat to redness until all carbon is gone. Weigh the precipitate as  $Mn_2P_2O_7$ . Dissolve the same in 1 : 1 hydrochloric acid, and if the solution contains any insoluble matter such as silicic acid, filter it out. Wash it. Ignite and weigh it. Deduct the weight from the weight of the  $Mn_2P_2O_7$ , multiply the remainder by 38.69 and divide by the weight taken for analysis to obtain the per cent of manganese.

\* Add only enough of the 1 : 1 ammonia, at first, to produce a slight milkiness. Stir the boiling solution until this milky precipitate becomes heavy and crystalline. Then add the balance of the ammonia, slowly, and with constant stirring to the boiling solution, making sure that an excess of ammonia is used.

If the quick nickel test (see Chapter IX, page 164) shows that considerable nickel or copper is present, these elements should be removed by hydrogen sulphide before making the phosphate precipitations. This can be done as follows: Make the filtrate from the iron hydroxide slightly acid with acetic acid and pass H<sub>2</sub>S through it until the sulphides collect and settle out well; filter; wash with H<sub>2</sub>S water; concentrate the filtrates and washings until crystallization begins. Dilute with enough cold water to dissolve the crystals; filter again; wash with water, alone, and then proceed with the phosphate precipitation of the filtrate as in the first gravimetric method.

#### VOLUMETRIC METHOD FOR MANGANESE.

Proceed by a bisulphate fusion as given for high manganese in insoluble ferro-titanium. Fuse 0.3 gram for 80 per cent ferro; 0.5 gram for 50 per cent and 1 gram for lower percentages of manganese.

For standardizing the permanganate solution it is better to weigh 0.3 gram of a ferro-manganese whose manganese content has been carefully determined by the gravimetric process. Put it through the entire volumetric operation, and, in this way, fix the value of the permanganate standard in milligrams of manganese, rather than by the standardization given on page 49.

#### PHOSPHORUS.

The precipitate of ferric acetate contains all of the phosphorus. It can be dissolved off the filter and evaporated to moist dryness on the *water bath*. Dissolve the residue in 50 c.c. of conc. nitric acid. Evaporate to about 5 c.c. Rinse into a 5-ounce beaker. Boil with permanganate and finish the phosphorus as in steel.

The phosphorus may be determined on a separate portion by dissolving 1 gram in nitric acid. Evaporate to dryness. Ignite to a dull red. Dissolve in HCl. Convert into nitrate. Filter and finish as in steels.

## SULPHUR.

' Sulphur is obtained as in steels by the gravimetric method.

## FERRO-SILICON, SILICON SPIEGEL AND METALLIC SILICON.

**Silicon and Manganese.** These high silicon materials should be fused with sodium carbonate and potassium nitrate. Fuse \* 1 gram with 20 grams of sodium carbonate intimately mixed with 4 grams of finely ground potassium nitrate. Dissolve the melt in water in a platinum dish. Transfer the green fluid and residue to a large casserole. Cover with a watch glass. Add an excess of concentrated hydrochloric acid, keeping the vessel covered. Clean the crucible with a few c.c. of the same acid. Add the cleanings to the acidulated fusion. Heat until all spraying ceases. Wash off the cover, allowing the fluid to flow into the casserole. Evaporate to dryness on a graphite or sand bath. Add 10 c.c. conc. hydrochloric acid. Warm, add 100 c.c. of water and heat for a half hour, or until all salt is dissolved. Filter. Wash the silicious residue free of chloride test. Evaporate filtrate and washings again to dryness. Dissolve, filter and wash as before. Dry the two residues obtained from the first and second filtrations. Roast off the paper from them at the lowest possible heat to prevent loss of silica. Then gradually raise the heat and blast the residues in a weighed platinum crucible until the weight of the ash is constant. Moisten the silica, which should be white, with a few drops of sulphuric acid. Fill the crucible nearly full of hydrofluoric acid. Add the latter cautiously, at first. Evaporate and finish for silicon as in steels. It is safer to evaporate a second time with hydrofluoric and sulphuric acids, using about one-third as much hydrofluoric acid as was used in the first evaporation, to make sure that all silicon has been volatilized.

\* Fuse 0.5 gram in an iron crucible with a mixture of 4 grams of sodium peroxide and 8 grams of sodium carbonate, if silicon, only, is required. Run blanks.

**Manganese and Iron.** The filtrate from the second evaporation to dryness should now be divided into two equal portions.\*

#### FIRST PORTION.

**Phosphorus and Sulphur.** Precipitate with a slight excess of ammonia. Wash the precipitate with water. Dissolve it off the filter with hot concentrated hydrochloric acid, using a little sulphurous acid if necessary. Convert this solution of the iron into nitrate; boil with a little permanganate and finish for phosphorus as in steels, calculating the percentage on a half gram basis.

**Sulphur.** The filtrate from the ammonia precipitation is made slightly acid with hydrochloric acid. The sulphur is precipitated with barium chloride and finished as in steels. Deduct a blank obtained on all of the fluxes and acids. If it is desired to use a larger amount of sample for sulphur, it can be determined alone on a one gram quantity without dividing into two portions.

#### SECOND PORTION.

**Manganese and Iron; Manganese.** This portion is evaporated to fumes with sulphuric acid. The iron is precipitated with ZnO and filtered out. The filtrate is finished for manganese as given for high manganese in insoluble ferro-titanium of high manganese content. (Page 52.)

**The Iron.** The iron and zinc oxide residues on the filter are dissolved off with hot sulphuric acid and reduced with zinc and titrated for iron in the same manner as given for iron in ferro-vanadium. (See page 29. See also page 368.)

**† The Carbon.** The carbon can be obtained by combustion of 0.5 gram of the ferro-manganese, etc., with 4 grams of red lead; or litharge is equally good as a substitute for the red lead.

\* The residue in the crucible after the volatilization of the silica with HF is quite likely to contain a little iron and manganese. It should be dissolved by warming with a little 1 : 1 HCl and added to the filtrate from the second evaporation to dryness before the same is divided into two portions.

† The carbon of ferro-silicon should be determined on a small quantity of the material on account of the great heat generated. Do not burn more than 0.500 gram at a time. Use 4 grams of the red lead.

## CHAPTER X.

### PART II.

#### RAPID VOLUMETRIC METHOD FOR MANGANESE IN THE PRESENCE OF IRON, CALCIUM AND MAGNESIUM.

THE usefulness of potassium ferricyanide in the determination of copper and nickel in steel, pig iron and ferro-vanadium led the author to investigate its quantitative application to the analysis of manganese. After considerable experimentation the following method was developed for manganese in ferro-manganese, and manganese steel. It is assumed that interfering metals, like copper, nickel and zinc, are not present in appreciable amounts: Pulverize a pound or two of 80 per cent ferro-manganese, and accurately determine its manganese content by the gravimetric methods as given. Use a ferro that tests practically free from nickel by the method described under Nickel in Steel, etc., pages 164-176.

*Method.* Weigh 0.5 and 0.6 gram of the standard ferro into 5-ounce beakers, and also the same quantities of the sample to be tested. Dissolve these portions with 50 c.c. of 1.20 nitric acid, keeping the beakers covered with watch glasses during the slow boiling. When the action is over and all of the samples are in solution, except perhaps a few brown particles of carbon (in the case of high-carbon ferros), remove the beakers from the fire. This is done before the solutions have concentrated to any extent. Cool and rinse one of the standards into a liter beaker. Add an additional 50 c.c. of 1.20 nitric acid to insure the presence of considerable salt. Dilute to 500 c.c. with water. Add 1 : 1 ammonia, little by little, with constant stirring, until the iron just begins to precipitate. Continue to add the ammonia, drop by drop, until the iron separates completely and settles. The solution should now smell but **VERY FAINTLY** of ammonia,

and have the characteristic rather sickening sweetish smell of a nearly neutral ammonia solution.

*Avoid Any Large Excess of Ammonia.* Mix with the hydroxide a thick cream of precipitated barium carbonate, free from copper. About 10 c.c. of this mixture of carbonate and water are sufficient. After stirring the carbonate through the iron hydroxide there should remain enough of the carbonate to form a white spot about the size of a dollar on the bottom of the beaker. The barium salt insures a constant SLIGHT excess of free ammonia, which is necessary to produce a rapidly settling precipitate on the addition of the ferricyanide standard. Add the latter slowly from 100 c.c. burette, at the rate of 100 c.c. every four minutes, stirring the contents of the liter beaker vigorously. A stirring rod is used with its lower end covered with a small rubber cap to prevent the cracking of the beaker. For high per cent ferros use a ferricyanide solution containing 15 grams of this salt to 2 liters of water.

The ferricyanide, at first, produces a nearly white precipitate with the manganese, in the slightly alkaline solution. This compound quickly changes to a brown color. As the end of the reaction between the standard solution and the manganese is neared, this flocculent precipitate collects and settles to the bottom of the beaker in 1 or 2 minutes. The substance turns bright blue on being mixed with a little ferrous iron in acid, acting in this respect like potassium ferricyanide. When all but 10 or 15 c.c. of the probable amount of standard solution needed have been dropped slowly into the beaker, *accompanied with continuous stirring*, stop adding the ferricyanide and stir vigorously for 60 seconds more. Lay the stirring rod across the mouth of the beaker with the rubber end resting on the lip of the same and projecting about an inch beyond. Place the index finger firmly over the other part of the rod and grasp the beaker with the rest of this hand. Now pour exactly 20 drops of the fluid through a 7 cm. filter into a 152.4 by 16 mm. test tube. If the filters are thin, use them double, for, if any of the brown precipitate were to run through, it would give an intense

blue with the indicator (ferrous chloride) and a false end point. When making these tests for end point, one should have, at hand, about two dozen test tubes. Do not use the same test tube for the next trial, as these tubes gradually get a coating on the inner surface that gives a faint blue color with ferrous salts. Clean the tubes that have been used for end point tests, first with water; then with concentrated ammonia to remove the coating; then with water to remove the ammonia; next with 1 : 1 hydrochloric acid; and, finally, with distilled water. The tubes are then ready for further end point tests. To the clear filtrate, in the clean test tube, add a few drops of ferrous chloride. Compare the blue color, if any is obtained, with that of a similar tint obtained as follows: In 800 c.c. of distilled water containing three drops of 1 : 1 ammonia, drop  $\frac{1}{2}$  c.c. of the standard ferricyanide solution. Mix thoroughly with a stirring rod. Pour just 2 c.c. of this mixture into a 152.4 by 16 mm. test tube, and add to it a few drops of the ferrous chloride. This gives a blue color of a DEFINITE depth of color. If the test gives a blue color that is lighter than the standard blue, then add another c.c. of the ferricyanide to the solution being titrated, and stir it swiftly for one minute. Have a watch at hand and stir exactly 60 seconds. If a blue color is now gotten that is deeper in shade than that in the standard tube, then stir the solution for 60 seconds more and again filter from it just 20 drops of solution. If this filtrate gives a blue with the ferrous chloride that is darker than the standard blue, the titration is considered complete, and  $\frac{1}{2}$  c.c. is deducted from the total amount of ferricyanide standard required. If the filtrate from the second testing gives a lighter blue, then 1 c.c. more of the standard ferricyanide is added to the solution being tested, and, after one minute's stirring, 20 drops are again filtered and tested with ferrous chloride. The blue of the test should now be quite a bit darker than the standard blue. Again the solution, being tested, is stirred 60 seconds and 20 drops filtered and treated with a few drops of ferrous chloride, which will most likely give a blue either matching the standard blue or a little darker. If the

colors match, make no deduction from the total cyanide used.

The object of the two stirrings and testings, after each addition of 1 c.c. of the standard, as the end point is near, is to make certain that the ferricyanide is not being still slowly combined with any manganese salt that may be occluded by the voluminous precipitate. This would be shown by the blue test, taken after further stirring, being fainter in color than the test taken at the preceding stirring.

As the blue tests seem to get darker on standing, the standard blue must be made fresh each time that a test is taken from the solution being assayed. That is, 2 c.c. of the 800 c.c. of stock are also taken and made blue with a few drops of ferrous chloride at the same time with each 20 drop test.

Suppose the standard ferro-manganese powder contains 79.8 per cent of manganese; that 216.3 c.c. were required of the standard to precipitate all of it and give the first and second blue tests: Then, if 0.600 gram of the standard ferro were taken,  $0.600 \times 0.798 \div 215.8 = 0.002218$ , or 1 c.c. of the standard ferricyanide solution equals 0.002218 gram of manganese under the *conditions as given*. This factor should be fixed by the operator.

One of the weights of the sample submitted should now be titrated exactly as described for the standard. If a result within 10 per cent of the standard is obtained, then that result is sufficiently accurate for all technical purposes; i.e., correct within less than one-half of 1 per cent in a possible 80 per cent. It is advisable to make the analysis in duplicate, and also the standardizations, using 0.5 and 0.6 gram in the case of 80 per cent ferro-manganese and correspondingly larger amounts of lower grade ferros. Should a very much lower percentage be found, for instance 42 per cent, then this finding is most likely 1 to 2 per cent too low. To arrive at the exact manganese, repeat the analysis so that the standard and the test contain as closely as possible the same amounts of iron and manganese in solution. For the example cited, weigh for standardizing pur-

poses 0.550 gram of the standard ferro, and in the same beaker also 450 mgs. of an iron, or iron wire containing 0.05 per cent, or less, of manganese. Of the sample to be determined weigh 1 gram. This gives a standard mixture and a test containing very nearly the same amounts of iron and manganese in solution. Proceed with the second analysis as outlined in the trial, obtaining a *higher* factor for the standard solution (1 c.c. = about 0.002318 gram Mn).\*

As the chemist usually knows, beforehand, within a few per cent, the percentage of manganese in the test, these trial analyses are, as a rule, not necessary. He needs only to observe the precaution of taking weights of the standard and of the tests so as to have, in each, approximately the same amounts of iron and manganese. For further illustration, suppose it is desired to assay a steel of about 13 per cent manganese. Allowing for about 1 per cent of other elements besides iron, 1 gram of such a steel would contain close to 130 mgs. of manganese and 860 mgs. of iron. To fix the manganese factor value of the ferricyanide for the titration of 1 gram of this steel, weigh  $0.130 \div 0.8$ , or 0.1625 gram, of the 80 per cent standard ferro-manganese and 0.84 gram of a low manganese iron into the same beaker. Titrate such steels exactly as the ferro-manganese except that a ferricyanide standard of one-half the strength of that given for ferro-manganese, or 3.75 grams to the liter, is advisable. And so on for steels ranging lower in manganese content, preparing standardizing mixtures from a standard steel containing from 12 to 15 per cent of manganese.

Ferricyanide standard solutions should be kept in the dark and standardized each day that they are in use. Clean the beaker and rod, after each titration, with 1 : 1 hydrochloric acid, rinsing out the acid with water before making the next titration.

Instead of standardizing with ferro-manganese, one can use c.p. permanganate of potassium and iron wire, making mixtures to almost exactly imitate the probable manganese and iron content

\* Read page 201.

of the test. For example, suppose it is desired to analyze, at the same time, a ferro about 90 per cent Mn, one about 43 per cent and one about 80 per cent Mn. For standard take 1.3 grams of c.p. crystals of potassium permanganate, and weigh also into the same beaker 0.500 gram of low manganese muck iron and 2.5 grams of oxalic acid. Cover the beaker and add a few drops of water. After the first violent action between the permanganate and oxalic is over, add, slowly at first, 50 c.c. of 1.20 nitric acid. Heat the beaker, and if the solution does not become perfectly clear, continue to add a few more crystals of oxalic acid. Heat until all brown flakes are dissolved. Then boil ten minutes; cool; and proceed as when standardizing with standard ferro-manganese. As explained, weigh, of the probable 90 per cent sample and of the probable 42 per cent sample, enough to give about the same amount of iron and manganese as in the standard mixture. Of the 90 per cent sample weigh, therefore, 0.500 gram together with 0.45 gram of the muck iron. (Electrolytic \* iron has but a trace of manganese in it, and should answer well as a source of iron.) Of the 42 per cent sample weigh 1 gram, but add no extra iron.

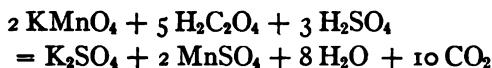
If the 1.3 grams of potassium permanganate require 193.8 c.c. of the ferricyanide to combine with it and give the blue end as described, then 1 c.c. of the ferricyanide, in the presence of approximately 0.500 gram of iron, has a manganese value of  $1.3 \times 0.994 \times 0.34777 \div 193.8$ , or 0.002318 gram. As the so-called c.p. permanganate of potash is often from 0.5 to 0.6 per cent short of 100 per cent purity, hence the introduction of the factor 0.994.

The determination of any amount of manganese in the presence of Fe, Ca or Mg can be accomplished, in duplicate, in 3 hours' time by this process.

The purity of the permanganate can be checked against recrystallized c.p. oxalic acid as follows: Dissolve 1 gram of the

\* Electrolytic iron of the following analysis can now be had: Phosphorus, 0.003 per cent; Sulphur, trace; Manganese, 0.02 per cent; Silicon, 0.003 per cent; Carbon, none.

permanganate in 150 c.c. of distilled water, acidulated with 100 c.c. of 1 : 3 sulphuric acid. Warm the solution *slightly*, and add to it 2.0167 grams of the oxalic acid, dissolved in 150 c.c. of distilled water. Warm the solutions a little, if necessary, until the mixture of oxalic and permanganate has become colorless. Titrate the colorless solution with a dilute permanganate standard of known oxalic value. The one used in the analysis of crucibles and plumbago answers very well. 1 c.c. of this standard equals 0.00144 gram of oxalic acid (see Analysis of Graphite, XVI, page 338). Suppose 25.5 c.c. of this standard are required to render the decolorized mixture a slight pink that will remain permanent for 30 seconds, therefore  $25.5 \times 0.00144$  or 0.0367 equals the excess of oxalic acid in the mixture. Hence  $2.0167 - 0.0367 = 1.98$ , or the amount of oxalic acid oxidized by the 1 gram of the permanganate. By the equation

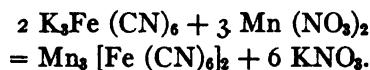


we have  $316.3$  grams of  $\text{KMnO}_4 = 630$  grams of  $\text{H}_2\text{C}_2\text{O}_4 + 2 \text{H}_2\text{O}$ , or oxalic multiplied by 0.502 equals permanganate;  $1.98 \times 0.502 = 0.99396$ , or the 1 gram of permanganate contains 0.9939 gram of 100 per cent  $\text{KMnO}_4$ . The precaution must be taken to use sulphuric acid that does not bleach permanganate on warming a few drops of the dilute permanganate standard with 150 c.c. of the acid.

In using potassium ferricyanide, it must be remembered that the action of the light produces a blue precipitate in it, and ferrocyanide forms which would give a blue with any little ferric iron that might be present in the indicator. At the close of the titration the solution must still smell faintly of ammonia, and an excess of barium carbonate should be visible in the bottom of the beaker. As long as the clear supernatant fluid clouds with 10 or 15 drops of the standard solution, after a wait of a half minute, the end point is still some 10 c.c. distant. As much as 0.500 gram of pure white marble together with 0.100 gram of metallic magnesium have been added, as nitrates, to

the solutions of nitrate of iron and manganese without any apparent effect on the titration of the manganese in the solution.

The reaction that takes place between the manganese and the potassium ferricyanide, in the slightly ammoniacal solution, is probably analogous to the one between ferrous iron and the ferricyanide:



#### FERROUS CHLORIDE SOLUTION.

This solution for making end point tests can be conveniently prepared from a low carbon steel with a copper content under 0.05 per cent. (If the steel contains too much copper, it will cloud with the ferricyanide.) Iron wire can be used. Dissolve 1.5 grams of the wire or steel in 20 c.c. of 1 : 1 hydrochloric acid, warming gently. When the solution is complete, add a few grains of granulated aluminum to entirely decolorize the iron. Then rinse the latter into a 500 c.c. stoppered flask and dilute to 250 c.c. with water. It is well to make the ferrous indicator fresh each day that it is needed. Decant the 2 c.c. portions of the indicator through a small filter to remove the excess of aluminum just before using.

The author proposes to work out similar quantitative volumetric methods for the assay of copper and zinc, as both elements combine speedily with the potassium ferricyanide in slightly acid solutions.

#### COMPARATIVE RESULTS BY VOLHARD, GRAVIMETRIC AND FERRICYANIDE METHODS.

	Gravimetric.	Ferricyanide.	Volhard.
Carbonless manganese.....	{ 91.51 91.66	{ 91.58 91.47	.....
High carbon ferro.....	{ 43.96 44.07	{ 43.74 43.68	{ 44.30 44.05
Manganese steel.....	13.00	12.90	.....

THE TITRATION OF SOLUTIONS FOR MANGANESE BY A STANDARD  
SOLUTION OF POTASSIUM FERRICYANIDE AFTER REMOVING  
THE IRON BY THE BASIC ACETATE METHOD.

After removing the iron by the basic acetate method, as given on page 188 and at the top of page 189, the combined filtrates are evaporated to 20 c.c. Then add 1 : 1 ammonia to the cold acetate solution until it will just turn red litmus blue and then add 10 c.c. of the ammonia in excess; titrate this solution with a standard ferricyanide made by dissolving 7.50 grams of this salt in water and diluting to one liter for ferro-manganese. One c.c. of this standard should equal about 0.002174 gram of manganese. For steels containing about 5 to 20 per cent of manganese, use a standard of 3.75 grams of the ferricyanide to the liter, which should have a value of close to 0.001087 gram of manganese per c.c. In the absence of iron the change of factor value required to compensate for the error due to the presence of iron is no longer required. In making the titration as given on page 194 the use of the barium carbonate is no longer required, and the end points are gotten with a saturated solution of ferrous ammonium sulphate instead of ferrous chloride. This is a very satisfactory titration but must be made in the absence of copper, nickel, zinc and cobalt which can be removed as directed on page 190 and the filtrate evaporated low to remove hydrogen sulphide, then filtered, this filtrate and washings are diluted by 200 c.c., and the analysis is finished as above. The titration is not interfered with by calcium, magnesium or barium and is therefore particularly advantageous in slag analysis. Chapter X, Part II, should be carefully read before proceeding with the titration. Standardizations are made by putting a weighed amount of c.p. permanganate of potassium together with about as much iron in the form of steel drillings (containing a known manganese content) as there is in the sample being analyzed through all of the above operations. The resulting acetate filtrate is titrated and the number of c.c. of the ferricyanide required to obtain the end point is divided into the manganese present in the perman-

ganate taken plus that contained in the steel drillings used to introduce the iron. The operator can also standardize by adding the main manganese in the form of standardized ferro-manganese. The manganese in the ferro can be determined by the method given on pages 188 and 189.

## CHAPTER XI.

### PART I.

#### THE DETERMINATION OF CARBON IN IRON AND STEEL BY DIRECT IGNITION WITH RED LEAD OR LITHARGE.\*

THE writer's experience with this method for the determination of carbon, together with some notes on what led to its adoption for routine combustion analysis, may prove of interest.

The solution of steel drillings containing large percentages of chromium, tungsten or molybdenum in double chloride of copper and potassium causes more or less loss of carbon as hydro-carbon. Especially sensitive to such loss are the carbides that are separated by the double chloride from steels in which are 10 or 12 per cent of molybdenum together with several per cent of chromium.

These carbides may lose some of the carbon by contact with dilute acid, or with the oxygen of the air during washing with *suction*, or during the subsequent drying of the carbide at the temperature of boiling water.

In the spring of 1900 the writer made an analysis for carbon of a steel containing 3.8 per cent of chromium, applying the ordinary method † of dissolving the borings in acid double chloride of copper and potassium, filtering on an asbestos plug, washing the carbide residue alternately with distilled water and a mixture of one part of hydrochloric acid and twenty parts of water. The residue was then washed with water, alone, to remove the acid. After drying the washed carbide in a water oven, it was burned with purified oxygen in a red hot porcelain tube containing about 13 cm. of copper oxide. The products of

\* A preliminary paper was read at the December, 1905, meeting of the Pittsburgh Section of the American Chemical Society.

† See pages 246 to 250.

the combustion were passed through granulated zinc of 20 mesh fineness, then through anhydrous calcium chloride, and then through phosphoric anhydride. The purified carbon dioxide was absorbed and weighed in potash bulbs. Duplicate analyses by this method failed to check.

A series of analyses of these borings were made. The acid wash *when used* was alternated with distilled water, and the washing was then completed with distilled water, alone, to remove acid.

	Kind of Wash.	Washings, Number.	Carbon Found, Per cent.
1.....	20 parts H <sub>2</sub> O to 1 part HCl.....	20	1.65
2.....	100 parts H <sub>2</sub> O to 1 part HCl.....	20	1.52
3.....	100 parts H <sub>2</sub> O to 1 part HCl.....	2	1.909
4.....	100 parts H <sub>2</sub> O to 1 part HCl.....	2	1.943

In August, 1902, the process used in the foregoing, (3) and (4), was applied to a steel containing 4 per cent of chromium and 4 per cent of molybdenum with the following absence of agreement:

First analysis gave 1.28 per cent carbon.

Second analysis gave 1.53 per cent carbon.

Third analysis gave 1.33 per cent carbon.

Fourth analysis gave 1.29 per cent carbon.

The thought occurred that perhaps the carbide obtained from molybdenum steel gives up part of its carbon as hydrocarbon on being brought into contact with the air during stirring. No heat was applied to hasten the solution at any time. A number of trial analyses were made in which the time of stirring was varied and also the acidity of the copper and potassium chloride solution. In the following, 2 grams of the drillings were dissolved in 180 c.c. of the double chloride solutions. By *acid* solution is meant a solution prepared by dissolving 600 grams of double chloride of copper and potassium in 1500 c.c. of distilled water acidulated with 175 c.c. of concentrated hydrochloric acid. By *nearly neutral* solution is meant the same as

the acid solution except that but 25 c.c. of concentrated hydrochloric acid were added to the 1500 c.c. of distilled water.

The *neutral* solution consisted of 600 grams of the double chloride, 1500 c.c. of distilled water, and *no* acid. The results obtained are given in the following table:

STEEL CONTAINING 4 PER CENT MOLYBDENUM AND 4 PER CENT CHROMIUM.

Kind of Steels.	Kind of Solvent.	Time of Stirring, Minutes.	Time in the Solvent with No Stirring, Hours.	Percentage of Carbon Found.
No. 1 steel.....	acid	20	.....	1.53
No. 1 steel.....	"	20	.....	1.48
No. 1 steel.....	"	10	.....	1.64
No. 1 steel.....	"	.....	12	1.49
No. 1 steel.....	"	.....	24	1.52
No. 1 steel.....	nearly neutral	8	.....	1.60
No. 1 steel.....	" "	8	.....	1.55
No. 1 steel.....	acid	3	.....	1.60
No. 1 steel.....	neutral	6	.....	1.593
No. 1 steel.....	"	6	.....	1.606
No. 2 steel.....	"	4	.....	1.679
No. 2 steel.....	"	6	.....	1.734
No. 2 steel.....	acid	4	.....	1.758
No. 2 steel.....	"	4	.....	1.66

A combustion of the 4 per cent chromium, 4 per cent molybdenum steel (No. 2), by the red lead process described below yielded 1.734 per cent carbon.

An examination of the foregoing table shows that both in the No. 2 and the No. 1 steels the highest result was obtained when the acid solvent was used, and also the lowest results.

Short stirring gave better agreements than the longer periods of stirring, but had evidently not eliminated all of the causes of loss. Perhaps there is loss of carbon when the carbide is being dried in the water oven. Further, it is practically impossible to regulate the suction so as to expose the residues, during washing, to exactly the same amount of air in each analysis.

Two grams of the No. 2 steel were stirred twenty minutes with 180 c.c. of the acid solution, then transferred to the asbestos

plug. Air was next drawn through the residue for fifty minutes; the amount of carbon obtained was 1.347 per cent. Two determinations of the same steel were made with sixty minutes' stirring but with the least possible exposure to air by suction; 1.63 per cent and 1.68 per cent carbon were found. In view of these results the practice was adopted of always keeping a layer of distilled water over the carbide during the washing. As soon as one layer, or covering of water, was drawn off, another was immediately supplied.

This treatment was applied to a group of ingots containing 11 per cent molybdenum and some chromium. The neutral solution gave the higher results, as shown by the following table:

Acid Solvent. Per Cent Carbon.	Neutral Carbon. Per Cent Carbon.
0.52	0.60
0.46	0.56
0.53	0.59

The same process of short stirring and least possible exposure of the carbide residue to air by suction, together with the use of a neutral solvent, was adopted for a series of ingots containing 12 per cent molybdenum and several per cent of chromium. It failed almost completely. For convenient comparison the results obtained in these latter experiments are shown in a column parallel to those obtained, at a later date, from the same samples by the red lead combustion method. (Page 207.)

One well-known laboratory obtained 0.72 per cent carbon, and another, equally experienced, reported 0.64 per cent carbon on the S. H. S. sample.

This untrustworthiness of the double chloride process for separating carbon in steel of high molybdenum and chromium content led to a search for some method of obtaining the percentage of carbon by burning the entire substance. Having about this time noted Brearley and Ibbotson's statement that steel

drillings that will pass a 20-mesh sieve and have been mixed with about three times their weight of red lead can be decarbonized in a red hot porcelain tube, it was decided to attack the molybdenum steel in this manner. The results obtained from the molybdenum steels are given in the table below and need no comment.

Sample. 12 Per Cent Mo. Steel Containing Cr.	Results Obtained by the Neutral Solution. Per Cent Carbon.	Results by the Red Lead Process. Per Cent Carbon.
No. 1.....	{ 0.54 0.72	0.80 0.79
No. 2.....	{ 0.81 0.51	0.76
No. 3.....	{ 0.66 0.49 0.51	0.82
No. 4.....	{ 0.54 0.58	0.81
" 2d trial " .....	{ 0.47 0.61	{ 0.88 0.85
No. 5.....	{ 0.61 0.88	{ 0.88 0.87
No. 6.....	{ 0.49 0.69.88	0.73
S. H. S.....	{ 0.66 0.68.75	
No. 7.....	{ 0.66 0.52	0.94 0.939
No. 10.....	{ 0.76 0.75 0.62	1.00
No. 11.....	{ 0.72 0.52	0.80

The method was first applied to plain carbon steels, pig iron, and white iron, and was found to be perfectly accurate.

After more than eighteen months' daily use of the red lead for the determination of carbon in steel, pig iron, alloy steels, and ferro alloys, the details that have been found useful and reliable are as follows:

If part of the borings are coarse, the thin curly portions or 30 to 60 mesh sievings are selected. Two grams of such drillings and 2 grams of the red lead are weighed into a glass stoppered

60 c.c. weighing bottle. The bottle is then shaken to mix the drillings and lead oxide.

The steel sample submitted for analysis is drilled with a flat or diamond pointed drill. This style of drill will grind many of the drillings to 20 mesh fineness in the case of soft or annealed steels. If the steel be unannealed and of a carbon content ranging from about 0.35 per cent carbon and higher, thin curly drillings are obtained which decarbonize readily by reason of thinness. If the drillings do not exceed 20 mesh, as in siftings, 4 grams of red lead will completely decarbonize 4 grams of the steel. Care is taken at all times to cover bulky drillings with the oxide of lead, as any drillings that project above the main body of the charge are likely to escape oxidation.

For soft steels and annealed steels two sieves are used. One has a 20 mesh gauze and the other one a 60 mesh gauze. Those drillings that pass the 20 mesh gauze but do not pass the 60 mesh sieve are used for analysis.

This arrangement rejects the fine dust and the thick drillings. When very small pieces of steel are received they are drilled with  $\frac{3}{16}$  inch diameter twist or straight drills. All sizes of the flat, or diamond point, drills are kept at hand from  $\frac{1}{4}$  inch diameter to  $\frac{7}{8}$  inch. Any good mill blacksmith can make the flat drills. By these means it is rarely, if ever, necessary to resort to the copper and potassium chloride separation of the carbon. In the laboratory of the Park Steel Co., where many combustions are made each day, covering a range from 0.04 to 3.5 per cent carbon, the writer does not recall more than a single instance in a year's time when it was necessary to resort to the double chloride process.

The mixture of lead oxide and drillings is transferred from the weighing bottle to porcelain boats.\* The Royal Meissen brand, 15 X 75 mm. or 112 X 12 mm., is mostly used, being convenient sizes. The porcelain boats are slipped into † por-

\* The author now uses the clay boats for all combustions, and clay tubes.

†  $\frac{4}{5}$  inch inside diameter fused silica tubes are very desirable for this work. The litharge fumes and spills, however, will, in time, destroy them. The writer sometimes uses a small inner cylinder of platinum just large enough to hold the boat. Iron oxide will flux silica tubes. (See clay tubes, page 243.)

celain tubes\* of 16 mm. inside diameter  $\times$  600 mm. long. Two furnaces with their porcelain tubes are operated at the same time. Until recently, the outlet ends of these tubes were filled for a distance of 125 mm. with granulated copper oxide. Later the copper oxide was found to be unnecessary. Oxygen is used during the combustion. It passes through a jar containing

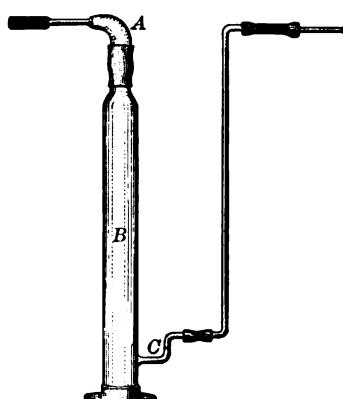


FIG. 4.

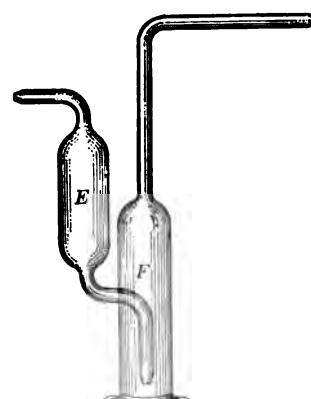


FIG. 5.

pieces of caustic potash (Fig. 4). It next bubbles through a solution of potassium hydroxide contained in a safety apparatus (Fig. 5), and is then dried in jars of soda-lime and calcium chloride of the design given in Fig. 4. This drying and purifying apparatus can be readily arranged and securely fastened in a space 250  $\times$  406 mm.

The combustions are operated in the usual manner. The portion of the tube containing the copper oxide is heated to redness, and then the remainder of the tube lying within the furnace is brought to the same temperature. The combustion tubes are constantly kept hot through half the length so that the combustion commences almost as soon as the stoppers are inserted. While the boats are being charged the oxygen is passing slowly through the tubes and the weighing and absorbing apparatus which has been previously weighed and attached.

\* The author is now using tapered clay combustion tubes. (See page 243.)

(This weighing apparatus is shown in Fig. 6. It was designed by the writer as a substitute for the different forms of potash bulbs now in the market. It is made of heavy glass. It is easily kept clean, is not top-heavy, and does not occupy much space in a balance case.)

As soon as the steel begins to burn, there is, at first, a rapid evolution of gas which quickly ceases. More oxygen is then turned into the apparatus from the steel cylinder so that a slow bubbling is maintained through the weighing apparatus. When the oxidation of the charge is completed, the oxygen begins to rush through the apparatus at a high rate of speed. The flow of the gas is quickly checked to a normal rate, that is, it is checked so that it passes through the safety apparatus (Fig. 5) at a rate of about 26 bubbles per 10 seconds.

The stream is evenly distributed to the two combustion tubes by means of a Y-tube and screw pinch-cocks. The stream passes through the weighing apparatus (Fig. 6) at the rate of 250 c.c. every ten minutes, which is the normal speed. When the combustions are completed in both sets of apparatus, as indicated by the passage of the gas at a high rate of speed, the normal is then maintained through the red hot tubes 10 minutes longer to insure complete oxidation and that all of the carbon dioxide has been carried to the weighing apparatus. The products of the combustion pass through a purifying train shown in Fig. 7. The train connects with the glass tube leading from the outlet end of the porcelain combustion tube, by means of heavy combustion rubber tubing, at *H*. The gases pass through the cylinder *I* which contains a column of granulated zinc of 20 mesh fineness. The use of granulated zinc to remove acid and chlorine in carbon combustions was first suggested by Dr. Edward S. Johnson. Cylinder *I* is 254 X 13 mm. The zinc is held in place with plugs of glass wool. The gases



FIG. 6.

next enter a cylinder *J* which contains a column of phosphoric anhydride. The phosphoric anhydride powder is held in place with plugs of ignited asbestos. Cylinder *J* is  $178 \times 13$  mm. Glass wool plugs should not be used in *J*, as they become clogged after a few combustions. Ignited asbestos is free from this objection.

The carbon dioxide, which is now freed from litharge and sulphur, and any acid fumes by zinc, and from any moisture

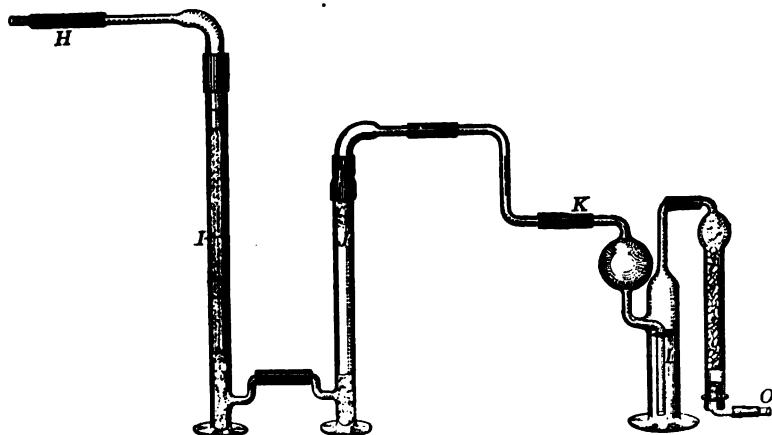


FIG. 7.

by the phosphoric anhydride, enters the weighing apparatus *L*. This weighing apparatus, as shown in the complete train (Fig. 7), differs slightly from the writer's first design shown in Fig. 6. The apparatus is charged with 20 c.c. of potassium hydroxide consisting of one part of caustic potash dissolved in 1 part of water. The drying tube *C*, Fig. 6, is filled with small pieces of *dry* caustic potash obtained by quickly cracking dry sticks of caustic potash in a porcelain mortar. Each end of the drying tube *C* contains a plug of asbestos or glass wool. Before inserting the rubber stopper in *C*, care must be taken to free the surface of the tube *C* from any moist caustic potash, as potassium hydroxide causes decomposition of rubber, resulting in continuous loss of weight.

The weighing apparatus is ready for recharging at the end of the fortieth combustion. The tare is then used for the absorbing and weighing of the carbon dioxide obtained from the next 40 combustions, the exhausted apparatus now constituting the tare.

During the passage of the oxygen the outlet *O*, Fig. 7, is protected from the ingress of moisture or impure air by a guard tube filled with small pieces of caustic potash. This guard tube is not shown in Fig. 7. All parts of the apparatus shown in Fig. 7 are connected by heavy wall pure rubber tubing.

When the combustions are completed the weighing apparatus is detached from its train, and the outlet of the train is closed with a glass plug.

It is accurate to weigh the absorption apparatus (Fig. 6) filled with oxygen and thus avoid aspirations. In this way combustions can be carried through in 25 minutes.

The apparatus and its tare are next carefully wiped with a clean linen handkerchief and are placed in the balance case for weighing. The inlet and outlet of the weighing apparatus are kept closed with rubber caps except during weighings or when attached in the train (Fig. 7).

The method of using an exact duplicate of the weighing apparatus for a tare exposes the same amount of surface to the air during weighings and avoids the use of the larger weights.

As previously stated the porcelain tubes are kept red hot throughout one-half their length night and day so that the combustion commences in a minute or two after the boat is inserted and the combustion tube is stoppered. The remaining burners are lighted immediately after the tube is closed.

\*The red lead used in this work must be thoroughly mixed and ground free of lumps before its carbon content is determined. The so-called pure red lead costing about 9 cents

\* On one occasion a lot of red lead was purchased that was not uniform. No amount of mixing improved it. It was rejected. Subsequent kegs gave no trouble. Good commercial red lead gives about 0.004 gram of CO<sub>2</sub> per 4 grams, and is very uniform.

per pound in 50 pound lots is found satisfactory for the purpose. Blank combustions with 4 grams of red lead are at present yielding 6 mgs. of carbon dioxide which are deducted from each determination. Blank combustions or analyses of standard steels should be made each day. The red lead is kept in tightly stoppered bottles.

The method of weighing the carbon dioxide obtained in the red lead combustions as barium carbonate was tried for several months. As it is not necessary to dry the carbon dioxide in this modification of the red lead method, the carbon dioxide was passed through a cylinder illustrated by Fig. 4 filled with granulated zinc to remove litharge fumes, and from thence the carbon dioxide entered the absorbing apparatus, which consisted of two  $254 \times 25.4$  mm. test tubes connected in tandem and containing barium hydroxide solution. The solution in the first tube converts the bulk of the carbon dioxide formed into barium carbonate, but in the higher carbon steels a little escapes into the second tube.

The barium carbonate is filtered through 12 cm. filters reinforced at the apex by a piece of cheese-cloth. The precipitate is washed 30 times with distilled water, allowing each washing to be drawn off by slight suction.

The cheese-cloth is removed and the precipitate is ignited and weighed. From this weight the amount of barium carbonate formed from the impurities in the red lead and that obtained from the unavoidable exposure of the excess of the hydroxide during filtration and washing is deducted. From the net weight of barium carbonate the percentage is calculated.

The barium hydroxide solutions are prepared by dissolving, or nearly dissolving, 200 grams of barium hydroxide crystals in 4 liters of water. It is filtered by suction through a paper pulp filter and preserved with the usual precautions. The test tubes for the solution are provided with 30 c.c. and 70 c.c. marks. The pair of tubes constituting the absorption pair are filled to the 30 c.c. marks with water, and the barium hydroxide solution is then poured in until the 70 c.c. marks are reached.

A protracted comparison of the two gravimetric processes described in this paper extending over a period of several months was made. The method whereby the resultant carbon dioxide was weighed as barium carbonate checked excellently with the one in which the carbon dioxide was absorbed and weighed in the apparatus shown in either Fig. 6 or in the termination of the train, Fig. 7, agreeing within 0.01 per cent or less. The latter (KOH) process is preferred as requiring less manipulation, less oxygen and less time. In the barium carbonate method it was necessary to force the oxygen through the safety apparatus (Fig. 5) at the rate of 38 bubbles per 10 seconds on account of the resistance to the passage of the gas through the absorption test tubes.

The ordinary 10-burner Bunsen combustion furnace is employed, but with certain alterations to secure higher heating power. At the points where the porcelain tubes rest in the ends of the furnace these ends are slotted down about 25 mm. This permits the tubes to lie well enveloped with the flames. Further, under each foot of the furnaces pieces of fire-brick about 28 mm. thick are placed. Also the rows of burners are lowered until they rest on the laboratory table. To keep the rows vertical one burner at each end of the rows is wired to the furnace. This lowering of the burners and raising of the furnace frame, by use of the fire-brick, improves the draught and secures hot flames with a minimum gas pressure. Strips of wet cheese-cloth about 25 mm. wide are wrapped around the ends of the porcelain tubes to keep the rubber stoppers from burning. The ends of these strips dip into suitable vessels of water.

Porcelain tubes glazed inside only, of 16 mm. inside diameter by 600 mm. long, will last from 6 weeks to 2 months when in use night and day. Flames are always kept under the tubes. Such tubes cost about \$3.00 each. (See clay tubes, page 243.)

Porcelain boats are cleaned for further use by allowing them to stand in nitric acid of 1.20 sp. gr. for some hours. The boats are ignited a few minutes in the flame of a Bunsen burner just before being used. Porcelain boats 14 to 15 mm. wide by from 70

to 75 mm. long, Royal Meissen brand, are quoted in 10 gross lots at \$14.50 per gross. These boats can be used 3 times.\*

The apparatus shown in Fig. 5 was designed as a safety apparatus to prevent the potassium hydroxide solution from blowing over into the rubber tubing from any cause. The oxygen enters the chamber *E* and bubbles through chamber *F*, which is filled to  $\frac{1}{3}$  its capacity with potassium hydroxide solution consisting of 1 part of caustic potash dissolved in 1 part of water. *F* is 35 mm. outside diameter by 170 mm. long. Fig. 4 shows a tower or jar that is used as a container for small pieces of stick caustic potash for purifying the oxygen. The pieces of apparatus shown in Figs. 4, 5 and 7 were designed by the writer to avoid the use of rubber stoppers.

†The following results attest the accuracy of the red lead process:

Name of Sample.	Weight of Sample Taken, Grams.	Weight of Lead Oxide Used, Grams.	Per Cent Carbon by Red Lead.	Per Cent Carbon by Double Chloride.
S. S. Co. carbon steel.....	3	9	0.0395	0.415
No. 690.....	.....	.....	0.985	0.96
No. 350, tungsten steel.....	.....	.....	1.285	1.29
No. 353, tungsten steel.....	.....	.....	1.338	1.354
No. 22, high per cent nickel steel.....	.....	.....	0.698	0.696
No. 14, nickel steel.....	.....	.....	0.447	0.450
S. XIX, high per cent tungsten steel.....	.....	.....	{ 2.40 2.39	2.35
Wash metal.....	1 $\frac{1}{2}$	1 $\frac{1}{2}$	{ 3.56 3.65	3.59
Wash metal.....	1 $\frac{1}{2}$	3	3.58	.....
C. B. pig metal.....	1 $\frac{1}{2}$	1 $\frac{1}{2}$	4.01	.....
C. B. pig metal.....	1 $\frac{1}{2}$	1 $\frac{1}{2}$	4.04	4.04
Soft O. H. steel No. 1.....	6	3	0.192	0.185
Soft O. H. steel No. 2.....	8	4	0.097	0.077
Soft O. H. steel No. 3761.....	6	3	0.156	0.145

In July, 1901, a sample of steel was sent by Sanderson Bros. Steel Works to several laboratories. The writer retained a

\* The author uses clay boats exclusively for carbon determinations.

† Reprinted from The Journal of the American Chemical Society (with additions), Vol. XXVIII, No. 7, July, 1906.

portion of these drillings for several years. The different laboratories reported as follows:

	Per Cent Carbon.
Atha Steel Works obtained.....	1.25
Crescent Steel Works obtained.....	1.20
Park Steel Works obtained.....	1.214
Spaulding Jennings Steel Works obtained.....	1.199
Sanderson Bros.' Works obtained.....	1.214
La Belle Steel Co.'s Works obtained.....	1.20
3 grams of this sample plus 1.5 grams of red lead burned in stream of oxygen gave.....	1.22

In March, 1901, the following parties reported the carbon of another sample of steel:

	Per Cent Carbon.
Booth, Garret & Blair reported.....	1.277
Sanderson Bros. reported.....	1.292
Park Steel Co. reported.....	1.301
Bethlehem Steel Co. reported.....	1.307
Crescent Steel Co. reported.....	1.315
3 grams of this sample decarbonized with 1.5 grams of red lead yielded.....	1.305

The writer has since had occasion to compare results with other laboratories covering a range in carbon from 0.32 to 1.45 per cent carbon with equally good agreements.

#### CARBON IN FERRO-CHROMIUM.

In applying the red lead process to ferro-chromium, it was found that the maximum carbon in the 65 per cent chromium alloy was obtained by burning the alloy with 3 to 4 times its weight of red lead. (See table at top of page 217.)

A red hot body of copper oxide hastens breakage of porcelain tubes by causing unequal cooling strains when the furnace flames are lowered or extinguished for any reason. Since February, 1 tube has been in use without copper oxide. The oxide is still retained in the companion tube, so that daily comparisons have been made.

## DETERMINATION OF CARBON IN IRON AND STEEL 217

Ferro-chrome.	Weight of Sample Taken, Grams.	Weight of Red Lead Used, Grams.	Per Cent Carbon Found.
Sample A.....	I	2	7.26
	I	3	7.54
	I	4	7.72
Sample B.....	1	3	7.73
	1	2½	7.03
	1	4	7.00
Sample C.....	1	2½	6.46
	1	3½	6.55
	I	1	6.05
Sample D.....	1½	¾	5.17
	I	2	6.403
	I	4	7.094
	I	3	7.15
Sample E.....	I	4	7.07
	½	4	7.18

In February, 1906, the copper oxide was omitted from combustion tube. The space ordinarily occupied with copper oxide was filled, loosely, with ignited asbestos. The following results indicate that the use of copper oxide in combustions with red lead is unnecessary:

Sample.	With Copper Oxide. Per cent Carbon.	Without Copper Oxide. Per cent Carbon.
3 square steel.....	1.479	1.477
No. 288.....	1.175	1.175
6 S.....	0.207	0.207
No. 1193.....	0.712	0.692
No. 7013.....	0.520	0.538
C. No. 2.....	1.48	1.51
No. 2703.....	0.316	0.309
No. 385.....	0.425	0.439
No. 7014.....	0.396	0.393
No. 7013.....	0.401	0.397
No. 1241.....	0.75	0.705
C. No. 3.....	1.281	1.283
No. 7015.....	0.409	0.407
No. 7016.....	0.481	0.478
No. 7017.....	0.312	0.315
No. 7018.....	0.425	0.43
No. 7020.....	0.431	0.431
No. 1200.....	0.73	0.75
Ferro-manganese.....	6.31	6.39
Mixture of plumbago and clay.....	45.96	46.04
Pig iron "B".....	3.61	3.58

Since writing this article the author has tried litharge as a substitute for red lead and has found that it possesses some advantages over the latter, being less destructive of boats and tubes. It is in general more pleasant to handle. Two grams of litharge to the same weight of steel are sufficient where siftings of from 20 to 60 mesh, or thin drillings that can be packed in a close mass, are obtainable. It is extremely rare that such a sample cannot be gotten if the chemist will only insist that a piece of the steel be sent to him instead of drillings that frequently are coated with a film of grease,\* or contain bits of paper, fine fibers of wool waste, leaf tobacco, blue steel, rust, scale, or clay. He can then take his own drillings with the proper absence of variety.† Most chemists are aware that the center of the cross section of a square bar or round piece of steel often contains as much as 50 per cent more phosphorus, sulphur and carbon than the outside part. Further, that sheet steel just as often varies as much in these elements, and *in spots*: Hence, to get an average and fair sample, a square bar or a round one should be drilled from the surface toward the inside, either halfway or all of the way through the sample when practicable.

If for any reason the steel must be drilled on end then a row of holes of *equal* depth should be drilled all of the way across the section and all of the drilling mixed together. In like manner a flat bar or sheet should have a series of holes of the same depth drilled across it from edge to edge. A failure to observe these precautions often results in disputes between buyer and seller.

\* Clean greasy or oily drillings by repeated extractions with ether. Place the drillings in a small weighing bottle and shake them up with enough ether to cover them. The ether will become yellow if the drillings are greasy. Pour this ether off. Pour on some clean ether and repeat the extraction; pour off, and so on, until the ether is no longer colored. This process removes lint at the same time, as one can readily notice. The fluid will be seen to be full of many short fibers, at times.

† Another cause of variable results is surface decarbonization, or bark. When steel shows bark all drillings should be rejected until the drill passes through the decarbonized zone. If the sample is too thin for this precaution, then the condition of the steel should be noted on the chemist's report. See pages 348 to 355 on the cause of bark.



FIG. 8.

It is surprising from what small and hopeless looking pieces of steel one can extract enough drillings of the proper cross section for direct combustion analysis with a good assortment of small drills and a little experience.

#### THE TAKING OF DRILLINGS OR MILLINGS SUITABLE FOR ANALYSIS.

In this connection one should read the remarks at the close of Chapter XI, Part 1. (Page 218.) Fig. 8 shows a drill press operated with a direct connected constant speed motor

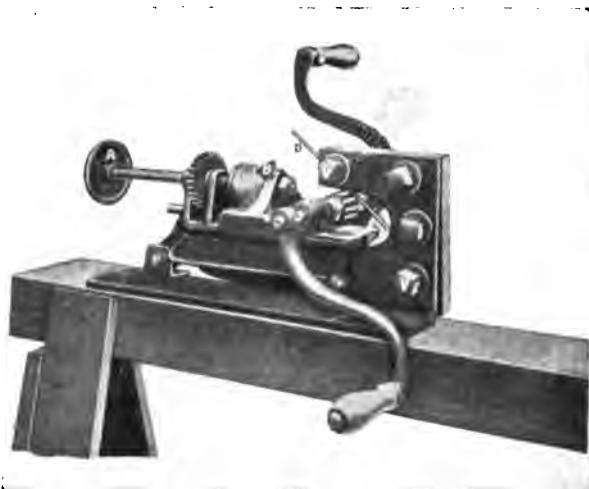


FIG. 9.

of  $3\frac{1}{2}$  horse power. The press is equipped with an adjustable vise which can be turned at any angle so that small and very irregular pieces of steel can be gripped and held immovable during the drilling. The drill chuck is large enough so that the set screw that holds the drill in place does not protrude, thereby preventing any possibility of the operator getting his sleeve caught and his arm twisted around the spindle. To prevent particles of oil or grease from getting in the drillings, thereby ruining the same for the determination of carbon by

combustion, the author had a large disk of sheet iron put on top of the chuck as shown. This precaution proved invaluable.

Fig. 9 gives the author's device for sampling material that cannot be drilled by reason of extreme thinness of cross section. At this writing quite a number of copies of this tool are in use both at home and abroad.

#### LABORATORY MILLING MACHINE FOR SAMPLING STEEL.

*Reprinted from Journal of Industrial and Engineering Chemistry.*

In certain kinds of steel the writer encountered much difficulty in getting samples of sufficiently small mesh for the determination of carbon by the direct method described by him several years ago.

The trouble was confined to thin sheets, wire, hack-saw steel, band-saw steel, razor blades, resistance ribbon, nails and small samples of all kinds that are irregular in shape and difficult to hold in the drill press vise.

The machine shown in the illustration afforded a successful means of avoiding various time consuming expedients.

The sample *D* of wire, for example, is held in the vise *V-V*. The millings are taken by means of a cutter, made of the best high-speed steel, and are caught on a piece of cardboard at *C*.

The automatic feeding device at *A* is hastened in its action by tightening the screw at *B*.

If millings are taken from very small gauge wire, a large sample can be obtained more quickly by twisting the strands together after cleaning the same with emery cloth, if rusty. In this way the cutter mills as many lengths as desired at one time. This machine mills copper wire with great ease. It makes easy the getting of the large quantity of material required for the determination of oxygen in copper, for example. In like manner, when it is desired to expedite the taking of large samples from extra thin sheets of metal, these sheets can be cut in strips with tinner's shears. The strips from the same sheet can then be laid one on the other, clamped in the vise, in layers, and all milled at once.

The milling cutter can be sharpened several times.

It is desirable, and well worth the small amount of time involved, to anneal all samples received, if they are not already in a softened state. This operation can be done in a half hour's time by heating the sample to 800° C. (bright red), quenching at once in water and then holding at 620° to 630° C., for 20 minutes (low red). Samples that cannot be quenched for any reason should be annealed as described under Annealing, pages 339 to 354. The annealing of 13 per cent manganese steel has also been previously described in "Analysis of Special Steels, etc., " together with the chemical tests for perfect annealing.

The millings obtained by this laboratory tool are not sifted, as they are just right for direct determination of carbon by combustion in oxygen.

If the sample submitted is sufficiently rigid, it does not need to be held by both ends, as in the case of the sample of wire.

This machine, as illustrated, has been in use in the writer's laboratory for a year. Since its introduction, the samplers no longer dread the appearance of wire and steel ribbon, this work being now a mere matter of easy routine.

The first cost was a bagatelle compared to the saving of labor in 1 month. Several copies of this milling tool are now in use in other laboratories of this company.

#### THE TAKING OF DRILLINGS OR MILLINGS.

##### *Hard and Soft Layers.*

Samples of steel are frequently submitted that consist of welded layers of hard and soft steel, such as soft-center, 3-ply knife, inserted and overcoat axe bit, jail-bar, and safe steel. Quite often when there are but two layers the hard one can be stripped from the soft one by placing the composite in a vise and driving a cold chisel between the layers. The hard strip can be annealed and milled. If stripping is not feasible, then the sample should be annealed and the hard portion drilled with a shallow, diamond pointed, wide drill of  $1\frac{1}{8}$  inch diameter at the wings.

If it is desired to drill a hard layer between two soft ones, the whole piece can be heated to bright redness and quenched in water. The soft layers can then be machined, or ground off. The hard center can then be annealed and milled.

It is a little more difficult to obtain drillings or millings from a soft layer lying between two hard ones. In such a case the cross section of the steel should be polished fairly smooth and etched with 1:20 nitric acid to clearly define the exact depth of the layers. The higher carbon zones will be plainly marked as black bands while the soft steel will retain its natural color. The sample is annealed before the etching is done, so that one of the black layers can be machined away. The white layer can then be drilled with a wide, flat drill.

In general it is a good thing to etch the polished section of samples, as often, by so doing, hard layers or insertions are discovered when least suspected; or curious defects, or spots or streaks, or segregations are revealed.

*Test for Segregation:*

Segregated steel becomes deeply pitted, in the segregated parts, on being suspended in sufficient 1:10 sulphuric acid to maintain a continuous evolution of hydrogen for several hours. Polish the piece fairly bright and smooth before making the test.

## CHAPTER XI.

### PART II.

#### THE DETERMINATION OF CARBON IN STEEL, FERRO-ALLOYS, AND PLUMBAGO BY MEANS OF AN ELECTRIC COMBUSTION FURNACE.\*

SEVERAL months ago it occurred to the writer that a special resistance wire could be applied to the heating of combustion tubes. A drawing was prepared for a furnace of a muffle type to heat four tubes lying in the same plane and parallel.

After some correspondence it was agreed at first to try a single tube furnace. It consists of a steel tube 295 mm.  $\times$  76.3 mm.

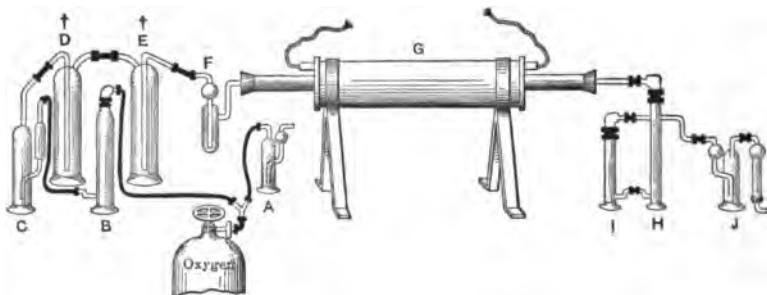


FIG. 10.

containing a non-conducting packing of magnesia oxide. In the center is a quartz  $\ddagger$  tube wound with the patent wire. Inside of this tube is placed another of the same material of 19 mm.

\* Reprinted from the Journal of the American Chemical Society (with additions), Vol. XXX, No. 5, May, 1908.

$\dagger$  In place of jars D and E, the shape B, Fig. 10, is used which has a wider neck and can be easily cleaned and refilled. That is, all three of these jars are the same size and shape as B. The cut on page 233 and the photo on page 242 show how this can be done. The contents of the respective jars are the same as before.

$\ddagger$  The author now uses a clay tube on which to wind the wire. He also is now trying wire wound directly on the tapered clay combustion tube.

inside diameter and 600 mm. long, in which the combustions are made.

- A. Mercury pressure gauge for detection of leaks and stoppages.
- B. Jar for stick potassium hydroxide or for any solid drier or absorbent.
- C. Safety jar for potassium hydroxide solution, preventing solution from backing over into rubber tubing.
- D. Calcium chloride jar.
- E. Soda lime jar.
- F. Mercury valve, to prevent reverse action, and absorb sulphur coming from rubber tubing. Note blackening of mercury after a time.
- G. Electric combustion furnace.
- H. Jar for granular zinc to remove
  - Acid fumes,
  - Litharge fumes,
  - Sulphur fumes,
  - Chlorine fumes.
- I. Jar for phosphoric anhydride to remove water.
- J. Absorbent and weighing apparatus for carbon dioxide.

The writer put in a small 32 ohm rheostat that happened to be at hand. With about  $\frac{1}{4}$  of this resistance the furnace, on a 220 volt direct current, has been maintaining a constant temperature. To secure complete combustion of steel it is very essential that the heat be maintained as close to 950° as possible, i.e., as little under that temperature as practicable. If the temperature drops to about 900° or under, the results obtained are liable to be from 0.01 to 0.10 per cent too low, unless red lead is mixed with the drillings. Hence, if one desires to operate with oxygen alone, the necessity of keeping the temperature from 940° to 960° Centigrade cannot be made too emphatic.

The oxygen is purified by passage through jars of stick caustic potash, potassium hydroxide solution, calcium chloride and soda lime in the order named. The oxygen then passes through a mercury valve into the porcelain or quartz (fused silica) or clay tube, half of which is filled loosely with ignited asbestos. The products of the combustion are purified from acid, sulphur, litharge or chlorine fumes by passing through a jar of granulated 30 mesh zinc. The water is removed by a jar of phosphoric anhydride.

For steels containing from 0.30 to 1.50 per cent carbon 2 grams of fine drillings, not over  $\frac{1}{4}$  mm. thick, are taken. For still lower percentages of carbon from 3.0 to 5.0 grams of drillings of not over 20 mesh size are selected.

The sample is weighed into a clay boat. The steel begins to burn by the time the stopper of the combustion tube is in place. Two grams of steel are decarbonized in 3 minutes and 5 grams in 6 minutes. The burning is continued for 10 minutes more with oxygen passing through the combustion tube at a rapid rate. The weighing apparatus is detached, wiped and weighed. Twenty-five minutes afford ample time for a single combustion, counting all operations.

The weighing apparatus and the jars for the purifying train are the writer's design, and were first published, in part, with illustrations, in the January *Journal of the Engineers' Society of Western Pennsylvania*, 1906, and more fully in the *Journal*, Am. Chem. Soc., 28, 862 (1906). This weighing apparatus *J* is used 40 times before it is refilled. As it is always weighed against a duplicate for a tare, after the fortieth combustion its tare is used as an absorber for 40 more combustions, so that when a pair has been freshly filled the operator knows he can complete 80 combustions before he needs to refill his weighing outfit. Do not fill *J* quite up to the bend of the inlet tube.

While no red lead is necessary for steel combustions, some of the alloys, such as ferro-chrome, carbonless chrome, and ferro-boron, require that red lead \* be mixed with the drillings or powder to break the metallic bond and permit of decarbonization. Ferro-chrome is the most refractory, as from a carbon content of more than 4 per cent only 0.2 per cent was obtained by burning as in steels with oxygen alone, at a temperature of 940°. Pig iron also requires some red lead. In general, about one-half the amount of lead required for decarbonization in a gas furnace is sufficient for the same work in the electric furnace, by reason of the higher heat attainable within the range

\* Or litharge.

of durability. A few of the many comparisons made in this laboratory between the combustions in a gas furnace with red lead and oxygen and combustion in oxygen alone are given in Table I:

No.	Sample.	Method.	Weight of Drillings Taken.	Amount of Red Lead Used.	Per cent Carbon Found.
			Grams.		
	1 Steel.....	Electric	4	None	0.09
"	1 "	Red lead	4	7 grams	0.09
"	288 "	Electric	2	None	1.176
"	288 "	Red lead	2	4 grams	1.175
"	2 "	Electric	5	None	0.121
"	2 "	Red lead	4	7 grams	0.111
"	3 "	Electric	1½	None	0.976
"	3 "	Red lead	1½	4 grams	0.967
"	4 "	Electric	3	None	0.109
"	4 "	Red lead	5	7 grams	0.118
"	5 "	Electric	2	None	0.469
"	5 "	Red lead	2	4 grams	0.474
"	6 "	Electric	2	None	0.736
"	6 "	Red lead	2	4 grams	0.737
"	7 "	Electric	3	None	0.118
"	7 "	Red lead	4	7 grams	0.117
"	8 "	Electric	2	None	1.17
"	8 "	Red lead	2	4 grams	1.168
"	9 "	Electric	2	None	1.15
"	9 "	Red lead	2	4 grams	1.16
"	10 "	Electric	5	None	0.046
"	10 "	Red lead	4	7 grams	0.040

The advantages of the electric heating apparatus are obvious. Very little heat is radiated; economy of space is attained; tubes are heated gradually and cooled gradually; time required is the minimum; labor cost is plainly the lowest because of simplicity and rapidity, and no expensive platinum tubes or boats or crucibles are used.

Some may say, "Why not burn the steel in air?" The answer is that the cost of oxygen is small, one-third cent per combustion, and the steel burns twice as fast. Oxygen can now be had at 1½ cents per cubic foot in 100 cubic foot cylinders. The method is accurate for all steels. As pointed out in the writer's

## FERRO-ALLOYS AND PLUMBAGO.

Sample.	Method.	Weight of Drillings Taken.	Amount of Red Lead Used.	Per cent Carbon Found.
		Grams.		
Tungsten powder.....	Electric	2	None	0.003
	Red lead	2	4 grams	0.010
Plumbago, No. 153.....	Electric	0.3	None	50.700
	Red lead	0.2	4 grams	50.800
Plumbago, No. 356.....	Electric	0.3	None	51.650
	Red lead	0.2	4 grams	51.300
Plumbago, No. 1.....	Electric	0.2	None	94.900
	Red lead	0.3	4 grams	94.300
68.5% ferro-chrome.....	Electric	1.0	1 gram	4.21
	Red lead	1.0	4 grams	4.15
Ferro-vanadium, No. 134.....	Electric	1.0	None	3.12
	Red lead	1.0	4 grams	3.09
Ferro-titanium, No. 1.....	Electric	2.0	None	0.22
	Red lead	2.0	4 grams	0.24
Ferro-boron, No. 1.....	Electric	1.0	1 gram	1.73
	Red lead	1.0	4 grams	1.72
{ Carbonless chrome, No. 9.....	Electric	1.0	1 gram	0.08
{ 96.0% chromium.....	Red lead	1.0	4 grams	0.09
Pig iron.....	Electric	1.0	None	3.20
" B ".....	Electric	1.0	0.5 gram	3.58
	Red lead	1.0	4 grams	3.58

article and in his preliminary paper read before the Pittsburg Section in December, 1905, one may lose as much as 50 per cent of the carbon in certain alloy steels by attempting to dissolve the borings in either neutral or acid double chloride of copper and potassium.

The best protection for the bottoms of clay or porcelain boats is a liberal layer of ignited silica sand,\* such as is used for acid open-hearth furnace bottoms. The silica rock is crushed to about 20-mesh and ignited in a muffle furnace at a bright red heat, cooled, and kept in glass stoppered bottles. Test the sand by a blank analysis.

To secure complete decarbonization it is necessary either that thin drillings be used, or if the sample contains much coarse

\* Read page 241 concerning the use of sand in combustion boats.

or bulky material, it should be selected. This can easily be accomplished by pouring the borings on a 20 mesh sieve and shaking all of the steel of 20 mesh size and the still more finely divided dust on to a 60 mesh sieve, which retains only the 20 to 60 mesh material. This *always* represents a good average sample.

Further, the drillings should be placed in as compact a mass as possible. If curly drillings are scattered along the entire length of the boat instead of being put in a deep, compact body, borings that are a little thick will frequently be found to still contain unburned metal. This detail is a very important one. Of course, the reason is that drillings lying in close contact heat each other to incandescence during the burning with oxygen.

Also, during the period when the oxygen is being absorbed in large quantity by the burning metal, the flow of the gas should be regulated so that there is an excess. That is, the oxygen must be turned on in sufficient quantity so that the gas is bubbling through the weighing apparatus slowly.\* However, if the gas is rushed through *J* during this period the steel becomes violently heated and slags with the sand and the sides of the boat, destroying the latter. Worse yet, low results are obtained frequently in this way, probably due to the formation of carbon monoxide, which is driven out of the hot portion of the tube before it is oxidized to the dioxide.

If the oxygen is turned into the tubes in sufficient quantity to maintain a slow stream during the period of the burning, the end point of the combustion is distinctly shown by a sudden increase of the speed of the bubbling through *J*. The rush of oxygen is then checked, but the rate of flow is still rather rapid for the final 10 minutes.

The weighing apparatus *J* is filled not quite to the bend of the inlet tube with a solution of potassium hydroxide made by

\* In order to maintain the slow bubbling through *J*, it is necessary to increase considerably the rate at which the oxygen is passing through *C* during actual burning of the metal to oxide. This also generates the required white heat in the steel at the critical time.

dissolving 500 grams of the latter in 500 c.c. of water. The drying tube at the outlet of *J* is closely filled with pieces of stick caustic potash cracked to about the size of a grain of wheat. To prevent the caustic potash from coming in contact with the small rubber stopper in the drying tube a *loose* plug of asbestos is placed at that point. The little bulb of this drying tube is filled about half full of glass wool. If dry sticks of caustic potash are cracked quickly, the small pieces can be conveyed to the drying tube in dry condition and constitute not only a splendid guard against loss of moisture from *J* but are also equally effective as an absorbent of carbon dioxide.

If a porcelain boat is used, the 15 × 75 mm. Royal Meissen boat is the best shape and most durable of any porcelain boats that the writer has tried.\* When putting in the sand bottom, fill the front half of the boat about  $\frac{2}{3}$  full and then with the butt end of the forceps make a trough in the sand, working it well up the sides of the boat. Pour the drillings from the weighing bottle into this depression. By so doing the drillings are kept in a compact mass, and when the combustion is completed the burned steel can be lifted out in a small cake. In this way a boat can be used from 10 to 15 times.

When a great many combustions are made daily, the fused silica, or electro quartz, tube is the most serviceable.† The continuous spraying of oxides against the walls of a porcelain tube weakens it, and when the current is turned off and the tube is permitted to get cold the contraction causes a rupture. Avoid spilling steel in a quartz tube.

To prevent the contents of *D*, *B*, *E* from clogging the inlets and outlets, large plugs of cotton are used at these points. Glass wool plugs should be used in *H* and loose plugs of ignited asbestos in *I*. Enough mercury is placed in the bottom of *F* and *A* to form a seal. The inlet end of the quartz tube heats somewhat, and it is better to wrap it several times around with a

\* The author now uses vitrified clay boats for all carbon combustions.

† Read page 232 concerning the vitrified clay combustion tube designed by the author.

strip of cheese-cloth, the end of which dips into a 150 c.c. beaker of water suspended directly underneath by means of copper wire. During the absorption of carbon dioxide the outlet of *J* is protected from ingress of moisture or carbon dioxide or fumes from the room by a drying tube not shown in the figure. It is filled with pieces of stick caustic potash broken to the size of a pea.

Oxygen can now be had, under high pressure, in 50-foot cylinders at about 2 cents per cubic foot, and in 100-foot containers at about  $1\frac{3}{4}$  cents per foot. The latter quantity will supply 2 furnaces, night and day, for 2 months.

**Gas Combustion Furnace with Blast.** The gas combustion furnace, described by the leading supply houses as "for draft or blast, with adjustable flame length" can be made very effective where compressed air is at hand. The author modifies it as follows: From the 450 mm. size take out one pair of tiles; shove the other two pair together into the middle of the furnace frame. Put the removed tiles on top of the remaining four to lessen radiation of heat. Close all of the burner shutters except the four middle ones. Let the inlet end of the  $\frac{1}{4}$  inch inside diameter, 30 inch electro-quartz tube project 12 inches beyond the tiles, and the outlet end 6 inches beyond the tiles. Fill the latter end, *loosely*, with ignited asbestos for a distance of 8 inches, beginning at the stopper. Wrap both ends at the stoppers with wet cheese-cloth as in the electric furnace. It is essential that the combustion tube be at least 30 inches long, and either of electro quartz or platinum, as with air blast and gas the furnace will heat the tube to from  $1150^{\circ}$  to  $1200^{\circ}$  C. in 20 minutes. This is in the range of temperature where it is possible to make direct combustions with air passing through the combustion tube instead of oxygen. Of course such a furnace is noisy and radiates quite a little heat, but is inexpensive.

In addition to the wet wrappings, with such extreme heat, it is safer, after putting in the charged boat, to follow it with a loose plug of ignited asbestos, placed in the tube about an inch

beyond the inlet end. This protects the stopper entirely from radiated heat. This plug can be used over again.

At  $1000^{\circ}$  C., using oxygen, coarser drillings can be decarbonized than at  $950^{\circ}$  C., and more quickly. Clay boats will not stand  $1100^{\circ}$  C. They crumble. Porcelain ones flux with the steel. Platinum boats are necessary at  $1100^{\circ}$  C.

When making combustions with air instead of oxygen, it is advisable to pass the gases formed through a second tube filled with copper oxide or some other catalyst heated to redness. Do not put oxide of copper in a quartz tube. It will flux it. A  $\frac{1}{8}$ -inch bore R. B. porcelain tube, 14 inches long, heated by a 5-burner Bunsen combustion furnace answers very well. With such a catalyst direct combustion of steel drillings, in air, is successful at about  $1150^{\circ}$  C. The author advises against combustions with air alone.

Burn heavy chips 1 hour.

#### THE DIRECT DETERMINATION OF CARBON IN STEEL, FERRO-ALLOYS AND GRAPHITE BY MEANS OF A COMPRESSED AIR AND GAS FURNACE.

Compressed air should be considered a necessity in all chemical laboratories, however small, where ignitions of any kind are part of the daily routine. With this great aid to combustion the furnace shown in the illustration (Fig. 11) can be made to heat a  $\frac{3}{4}$ -inch bore fused silica tube to from  $1150^{\circ}$  to  $1200^{\circ}$  C. in from 15 to 20 minutes. The cut shows the writer's modification of the original arrangement of the tiles. One pair of the latter is removed from a \* 495 mm. furnace; the other two pair are shoved together into the middle of the furnace. The removed tiles are placed on top of the middle pair forming an arch at *P*, *P*.

The vacant spaces at either end of the frame are packed with asbestos wool. All of the burner shutters are kept closed except the four middle ones at *O*. To permit the flame to pass up freely, the tiles are separated about  $\frac{3}{4}$  inch at the bottom, *M*'', *M*'''

\* No. 17 furnace, 18 inches long.

and  $\frac{1}{4}$  inch at the top,  $M$ ,  $M'$  (Fig. 11). This is easily accomplished by sliding  $\frac{1}{2}$  the iron frame up the inclined iron supports. One can readily adjust the air pressure and the gas at the points indicated to produce 950° C. in ten minutes. The

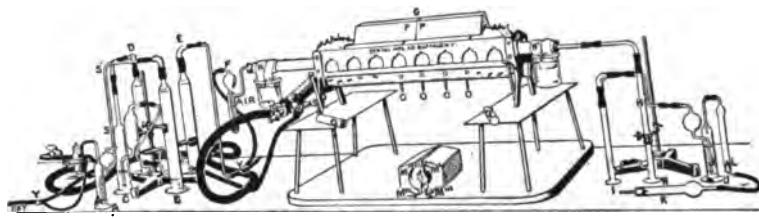


FIG. 11.

Showing the Fletcher Tube Furnace as modified by Charles Morris Johnson and fitted with his combustion train.

range between 950° and 1000° is best for the work. To provide for variations of air pressure a small regulator is located at  $R$ . This regulator is inexpensive and can be bought from any concern supplying pressure faucets.

To prevent the cracking of the fused silica (electro-quartz) tubes when using this furnace for the determination of carbon in steel by the direct combustion of the drillings in oxygen, a small inner sleeve or tube of platinum should, by all means, be at hand. If the quartz combustion tube be heated much above 950° C. and a single drilling is spilled in it, or the highly heated steel cuts through the clay or porcelain boat, the oxide of iron forms slag with the silica of the tube and the latter will soon crack. To avoid frequent and expensive breakage of combustion tubes from this cause the writer, in 1906, designed the small cylinder of platinum shown at  $Q$ ,  $Q'$  (Fig. 11).  $Q$  shows the open end of the same and  $Q'$  gives a view of the closed end of the cylinder. One-half of this end is perforated with small holes. It is 125 mm. long and 18 mm. in diameter. It can be made to weigh not over 30 grams and at a cost of about \$28.00.\* The cylinder is kept in the combustion tube. To receive the

\* The present high price of platinum makes this cylinder undesirable.

charged boat and for the removal of burnt residues this holder is drawn nearly but not quite to the entrance of the quartz tube. Keep it just a little back of the stopper. The clay boat into which the steel drillings are poured, in a little pile, is slipped into the cylinder and the combination is quickly pushed into the hottest part of the combustion tube. The tube is stoppered as rapidly as possible and oxygen is immediately turned in with sufficient volume to maintain a medium rate of bubbling through the absorbing and weighing apparatus *J*. As soon as the steel gets heated, it begins to absorb oxygen in large quantities as shown by the slackening of the rate of bubbling through *J*. It is highly important to continue to turn in more of the gas so as to always maintain an excess of it or low results will be obtained. Increase the flow of the oxygen through *C* so as to keep up a fairly rapid stream of gas passing through *J* during the absorption period. When the burning is completed, which occurs in about 5 minutes after the tube has been stoppered, the oxygen will begin to rush through *J* at a high rate of speed. The flow is now checked to the normal which is still quite rapid as but 10 minutes more are allowed to complete the combustion of 2 grams of steel and carry all of the  $\text{CO}_2$  over into the weighing apparatus *J* (Fig. 11). Allowing 2 minutes for the final weighing, an accurate combustion of steel drillings can be made in from 20 to 22 minutes. The writer operates furnaces in pairs by a 2-way connection. This still further reduces the average time per combustion, counting all operations except the drilling of the sample.

The second furnace is placed parallel with the one shown in the cut. The air pressure for this extra furnace is bled from a cock on the furnace, shown at *A* (Fig. 12). It is the middle one which is closed in the illustration (Fig. 11). The air is conducted from this point to the same cock on the additional furnace by heavy pressure tubing. In this way air for 2 furnaces can be supplied from one regulator at *R*. By similar means, through a *Y* not given, gas can be furnished from the 1 gas nipple located near *R*.

The oxygen is turned in at oxy. (Fig. 11) and is distributed at the first *Y* to the pressure gauge at *A* which contains a little mercury. It serves the 2-fold purpose of indicating stoppages and leaks. If there be a stoppage, the mercury will rise to an abnormal height in the tube that dips under the mercury in *A*.\* To test for leaks, plug with a glass rod the outlet end of the purifying train at the point where the absorption and weighing apparatus *J* is shown attached. Then turn on the oxygen until the mercury rises in *A* to the first bend of its outlet tube. Then shut off the oxygen: If there be a leak beyond *C* in the direction of the furnace, the mercury will slowly drop and the slightly compressed oxygen will bubble very slowly through *C*, if the leak be a small one. But, if the leak be somewhere between *C* and the oxygen tank in the direction *BS'S*, then instead of there being a bubbling through *C*, the fluid in the latter will recede from the bottom of *C*, rising up into the side bulb of *C*. The valves on oxygen tanks frequently develop leaks and the little gauge at once calls attention to the fact if this test is made. *C* is filled to the distance shown in the drawing with a solution consisting of 250 grams of caustic potash dissolved in 250 c.c. of distilled water. The oxygen, after passing the first *Y*, enters *B* via the glass tube *SS*. It then passes down through *B* (Fig. 11) which has a loose plug of cotton at the top and is filled with short pieces of stick caustic potash. The gas leaves *B* at the bottom outlet and enters *C* via the S-shaped glass tube. The gas bubbles through the fluid in *C* and enters *D* at

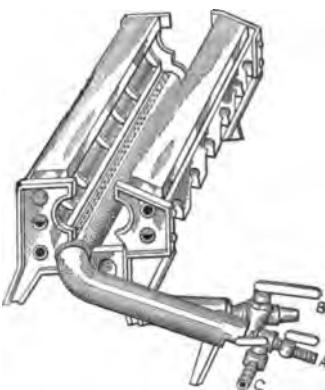


FIG. 12.

No. 17 Furnace open ready for the introduction of a tube.

\* When 2 furnaces are in operation the required pressure in *A* will cause the mercury in it to rise to a height of about 35 mm. It is a great advantage to have 2 furnaces. One checks the results obtained in the other.

the top where there is a loose wad of cotton. *D* is filled with alternate layers of anhydrous calcium chloride and cotton. The gas leaves *D* at the bottom outlet and enters *E* at its bottom inlet. *E* is filled with alternate layers of cotton and soda-lime. The bottoms of the jars are filled with loose plugs of cotton to prevent the clogging of inlets and outlets by these salts. The oxygen travels up through *E* and, by way of a glass tube, can be distributed to the pair of combustion furnaces at the second *Y* tube.

The combustion tube is of fused silica, or electro-quartz. It is 30 inches long and projects 12 inches beyond the furnace frame at the inlet end and 6 inches beyond the frame at the outlet end. It is filled loosely with ignited asbestos for a distance of 8 inches beginning at the outlet end. Both ends of the tube are wrapped at the stoppers with wet cheese-cloth, the ends of which dip into beakers filled with water as shown at *N*, *N'*. The products of the combustion are purified from litharge, sulphur, chlorine and acid fumes by a jar of granulated zinc of 20 mesh fineness (*H*). The gases are further dried by passing *up* through a jar of  $P_2O_5$  powder (*I*). "*I*" has a loose plug of ignited asbestos at the bottom of it and a similar one at the top. The pure  $CO_2$  is now received into the weighing apparatus *J* which is filled with the same kind of solution as given for *C*, halfway to the bend of the tube that dips into it. The guard tube *L* is filled with small pieces of dry caustic potash prepared by quickly breaking the dry sticks in a porcelain mortar to about the size of large grains of wheat.\* Reject the dust and use it for the absorbing solution. Such a tube makes a most effective guard against loss of moisture from *J* and also acts as a further absorbent of  $CO_2$ . This apparatus *J-L* is good for 40 ordinary steel combustions at a rapid speed. It is weighed against a mate and thus 80 combustions are obtained from a pair before refilling is necessary. *D*, *B*, *E*, *I* and *H* are refilled by removing the glass goose necks. The tube *K* is filled with the same material as *L* and prevents

\* The bulb of *L* is filled with glass wool. The little rubber stopper is protected from the pieces of KOH by a loose wad of ignited asbestos.

any suction of impure air into the weighing apparatus during the process of a combustion. The writer designed the entire train several years ago with a view to reducing the use of rubber stoppers to a minimum and to provide a convenient form of weighing apparatus for carbon dioxide. When using *J-L* for the determination of carbon in plumbago (natural graphite) it is replenished when 3 grams of CO<sub>2</sub> have been absorbed.

It is important that the small tube that dips into the KOH solution in *L-J* be not less than 6 mm. outside diameter and that its internal diameter be not reduced as it is very necessary for rapid work that it deliver large bubbles to the absorbing fluid.

In ordering quartz or fused silica tubes the chemist should specify that the ends be fused smooth, free from inside chipping and grooves, and of practically round bore, otherwise he may have unpleasant experiences with leaks at stoppers. He should further insist that the tubes be of full  $\frac{3}{4}$  inches inner diameter for at least  $\frac{3}{4}$  of the length, or his small platinum cylinder may stick in the tube.

Care should be taken to keep the heat of the furnace very little in excess of 1000° C. as combustion with oxygen at higher heats will cause the drillings to flux with the boat, cut through the latter, and at times stick to the platinum sleeve. The operator will soon learn to judge the proper heat without a pyrometer: If on drawing out the boat he finds nothing in it but a fused slag and that, perhaps, the latter has cut through the boat, then he has been working at a temperature in excess of 1000° C. If he finds a residue that is a dull black mass of oxide which can be broken off short in his fingers, does not present more than a slight melted appearance on top and does not contain particles of unburned steel, then the temperature of the furnace is just right. If the residue instead of being of a dull lustrous jet black has a slightly reddish appearance, the combustion has been made at too low a heat and the decarbonization is incomplete. If the combustion tube presents a white hot appearance, inside, the heat has attained to 1200° C. If the heat has a dazzling effect the temperature is still higher.

A yellow heat, viewed in the bright daylight, is about  $920^{\circ}$  to  $980^{\circ}$  C.; a bright yellow, suggesting the first appearance of whiteness, is about  $1150^{\circ}$  C. By exercising a little care in adjusting the air and gas supply this furnace can be operated with very little noise or radiation of heat and yet develop from  $950^{\circ}$  to  $1000^{\circ}$  C., which is ample for direct combustion of steel in oxygen. A small milling attachment should be on every drill table, such as is used in "gumming" saws. In this way finely divided millings can be obtained from thin sheets, wire and razor blades. The writer uses  $\frac{1}{8}$  pitch cutters that are held in a chuck in the same manner as a drill. The sheet or wire is clamped to the drill table and is shoved against the milling cutter which is revolving horizontally. The writer now uses his milling machine (see page 220, Fig. 9).

The drillings or millings, which should be either very thin, medium size, curly ones or should pass a 20 mesh sieve if from soft or annealed steel, are put in the boat in as compact a mass as possible. The drillings should not be scattered. Do not try to remove the residue after a combustion. Put in the next sample in a little pile and as close as possible to the oxide remaining from a previous analysis. In this way from 4 to 5 carbon determinations can be made in a clay boat without bothering with a sand bottom. Of course porcelain boats can be used for this work but they are more expensive and do not last any longer than a well made clay boat. Sand should be used to protect the bottoms of the porcelain boats. Well ignited silica sand, such as is used in furnace bottoms, is suitable. As stated the writer has found that, with a little practice in manipulation of the gas and air pressure, the furnace shown in the cut can be made to heat to from  $1000^{\circ}$  to  $1050^{\circ}$  C. with very little noise and radiation of heat. On the other hand it can be run with much unnecessary racket. In this laboratory natural gas is used at a pressure of 8 ounces. A moderate air pressure is sufficient, i.e., about 30 pounds.

When making direct carbon combustions of pig iron in oxygen, shake up with the 1 gram of sample half this amount of red

lead or litharge to break the bond between the iron and silicon. This secures complete combustion of pig iron. For refractory substances like ferro-chrome, carbonless chrome, silicon carbide, metallic silicon and ferro-boron, weigh 1 gram of sample and mix the same with 4 grams of litharge. Put this charge in a clay boat and proceed with the combustion as given for steels. Deduct a blank due to the CO<sub>2</sub> obtained from the lead oxide. It is safer to follow this plan for tungsten and molybdenum powders, ferro-silicon, ferro-vanadium, ferro-titanium and ferro-molybdenum. All varieties of plumbago or natural graphite that the writer has analyzed in connection with the plumbago crucible factory of this works, when finely ground as described in his methods for the analysis of graphite, burn completely to CO<sub>2</sub> in oxygen. Some of the finer grades of the natural concentrated product yield 99 per cent pure carbon. It requires about 45 minutes to completely burn such material.

When using red lead or litharge to secure complete combustion of the carbon in ferro-alloys rich in aluminum or silicon, or both, the charge is placed in one end of the clay boat *without* a sand bottom. After completing the combustion which proceeds just as quickly as that of a steel with oxygen, alone, the used part of the boat is broken off and the other half is then taken for further combustions. The best way to determine the blank, due to the lead oxide, is to burn 2 or 4 grams of it with some 20 to 30 mesh siftings of a steel, the carbon content of which is accurately known; or with 2 grams of small thin curly drillings of some standard steel. The excess of carbon found is the blank due to the lead oxide. A good "C. P." or commercial red lead or litharge will give a blank of about 0.004 gram of CO<sub>2</sub> per 4 grams of lead oxide.

L-J is wiped off with a piece of clean cheese-cloth or a clean handkerchief before each weighing of it. Its outlet and inlet ends are kept closed with small rubber caps when it is not connected in the train. These caps are removed during weighings. Not more than 2 minutes are spent in weighings at the end of the combustion. One minute is sufficient to weigh the drillings

at the start. One or two minutes more may be consumed in transferring the boat to the combustion tube and connecting *L-J* in the train. But 15 minutes are required to burn the sample and carry all of the CO<sub>2</sub> to *L-J*. In this way perfectly accurate combustions of all kinds of steels, either plain or alloyed, with any amount of tungsten, molybdenum or chromium can be carried through in 20 minutes. This is the routine practice in this laboratory when making bath tests of open hearth heats before same are ready for tapping.

This furnace has one marked advantage over electrically heated furnaces, in that it can be brought from a cold state to 1000° C. in 10 minutes. It can also be adjusted to fit any size combustion tube. (See Fig. 12.)

## CHAPTER XI.

### PART III.

#### FURTHER NOTE ON THE DETERMINATION OF CARBON IN STEEL AND FERRO-ALLOYS.

##### SURFACE DECARBONIZATION.

REFERRING to remarks on page 218 relative to the taking of samples it must be noted that steel often has a decarbonized surface, that is from 10 per cent to almost any amount lower in carbon than the main body of the metal. This will often cause the chemist to report the rolled or hammered steel anywhere from 0.10 to 0.20 lower in carbon than the original ingot analysis, that is, suppose the ingot analysis was 1.20 per cent carbon then it not infrequently happens that the plate or bar may show but 1.10 per cent.

##### USE OF SAND IN BOATS.

The author no longer uses any sand in the combustion boat as the composite vitrified clay boat is greatly superior and withstands a much higher heat than the original form of clay boat. By avoiding extreme heats during the combustion, complete decarbonization can be effected without fusing the drillings to the boat, and the little pile of sintered oxide that remains after the burning can be scraped out with the tail of a small file. If the combustions are run at a high heat with the drillings in contact with a sand bottom there is danger of forming silicon carbide as has been pointed out by Mr. Geo. M. Berry.

##### OXYGEN VERSUS AIR IN DIRECT COMBUSTION.

Since writing the first edition of this book the price of oxygen has fallen to less than 2 cents per cubic foot so that there is no longer any inducement to try direct combustions in air. In



Photo No. 13.

any case the high temperatures necessary make such combustions very unpleasant and should be avoided.

#### TWO PARALLEL FURNACES.

Photo No. 13 shows the author's arrangement for two combustion furnaces, side by side.

#### THE GAS COMBUSTION FURNACE WITH BLAST.

On page 233 the above direct combustion method is referred to. It constitutes a very cheap and effective way of making direct combustions. The principal objection to this method of heating is that the sharp, bare flame of the compressed air furnace striking the fused silica tube causes the latter to become devitrified and leak after some time.

#### THE ELIMINATION OF RUBBER STOPPERS FROM THE VITRIFIED CLAY COMBUSTION TUBE BY MEANS OF TAPERED CLAY INLET AND OUTLET.

*Received June 13, 1913.*

BY CHAS. MORRIS JOHNSON.

IN this journal, 5, 488, the writer published an account of a vitrified clay combustion tube with tapered outlet designed by the author and manufactured at this works. The tube has been in successful operation for 6 months of 24 hour working days and is still in commission. Several more are now in use and mark a considerable reduction in cost of carbon determinations as the material from which the tubes are made costs less than 1 cent per tube.

The advantage of the tapered outlet very soon suggested the making of a tapered clay inlet which is shown at *K* in the illustration and also at *L-M*. (Fig. 14.)

The clay part of the inlet is a duplicate of the outlet end. The tube is charged and discharged by removing *L-M* which is connected to the main part of the combustion tube by means of the rubber sleeve *M*. This connection is a piece of  $\frac{3}{4}$  inch bore,



FIG. 14.

$\frac{3}{16}$  inch wall and  $2\frac{1}{4}$  inches long, pure rubber tubing. This sleeve is more easily handled than a rubber stopper. The operator grasps *L-M* at the clay part *L* and slips it over the main part of the combustion tube and twists it firmly in place. The clay part *L* offers a substantial hold for one's hand and is absolutely safe. A glass taper would be dangerous as it might be crushed when grasped, causing a wound.

The slip-over connection is geometrically a tighter connection than a rubber stopper, for the reason that the latter affords an example of a conical surface pierced by the cylindrical surface of the combustion tube which makes only a single circle of contact between the stopper and the tube. The slip-over gives a tangential contact which provides innumerable circles of contact.

Further superiority of the tapered clay and rubber sleeve inlet is that, should the bore of the combustion tube tend to be elliptical instead of a true circle, the elasticity of the rubber sleeve will still give a pressure tight connection on account of the large surface of contact.

Again, many combustion tubes offered by dealers are rejected because of grooves in the interior walls, at the inlet or outlet ends, which make tight connections with rubber stoppers impossible. The tapered slip-over connection renders such tubes perfectly satisfactory.

The entire apparatus with the single exception of the little mercury valve tube attached to *L-M* is the author's design and shows but one rubber stopper at an unimportant point in the little KOH drying tube at the extreme outlet end of the combustion train. This could also be eliminated by a small glass taper or clay taper. The wet wrapping can be omitted, entirely, when the clay tube is used, although shown in Fig. 14.

It has been found in the author's experiments that, for a given wiring, furnaces heat higher with clay tubes than when fused silica tubes are used as there is less leakage of heat via the tube when the clay tube is in the furnace.

## CHAPTER XI.

### PART IV.

#### THE DETERMINATION OF CARBON IN PLAIN STEEL AND IN ALLOY STEELS, CONTAINING NOT OVER ONE OR TWO PER CENT OF ALLOYS, BY SOLUTION IN COPPER AND POTASSIUM CHLORIDE.

THE limitations of this method cannot be absolutely fixed as the carbon can be accurately obtained on certain alloys that have a greater amount of the non-ferrous metals than given in the above title; notably nickel steels can be accurately determined for carbon where the nickel content is far in excess of 2 per cent. The reader should refer in this connection to pages 203 to 207. Occasionally the chemist receives thick chips that are impossible by the method given on the pages just mentioned, and rather than wait for a more suitable sample or perhaps put a good customer to the inconvenience of getting drillings of the proper fineness, the analyst will resort to the double chloride method. The details are as follows:

#### THE DISSOLVING SOLUTION.

The acid solution given on page 204 is used for this work. It is filtered on ignited asbestos. The latter is prepared by igniting the fine white fiber in a muffle furnace in a porcelain dish. The dish is filled heaping full and brought to a bright red; it is then removed from the furnace and allowed to cool below redness. The lump of partially ignited asbestos is turned over and the dish and its contents are returned to the furnace; again brought to bright redness; and so on until the asbestos has been heated and cooled three times. While the asbestos is cooling it should be covered with a clean agate ware pan to prevent soot or carbonaceous dirt of any kind from falling on

the asbestos. The ignited asbestos is cut into short wads; put into a glass stoppered, carefully cleaned quart bottle and enough distilled water mixed with it to make a rather thick pulp.

The pulp is poured on a perforated porcelain plate of at least 2 inches diameter which is kept from slipping out of level by applying slight suction while the filter is being prepared. The asbestos is distributed over the plate in an even layer about 1

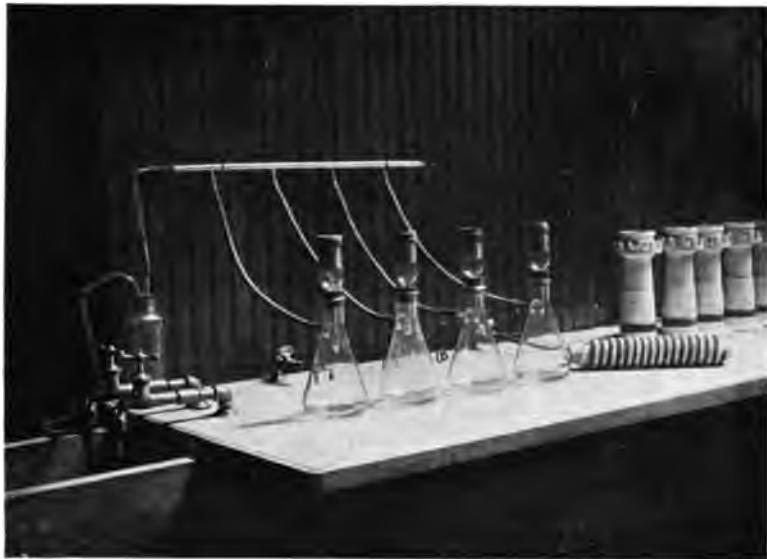


PHOTO No. 15.

inch thick and is put firmly to place by increasing the suction a little and pressing it down with a glass rod. (One end of the rod is flattened into a disk by softening it in the flame of a Bunsen burner and quickly pressing it against a cold surface.) Repeat this operation, adding, in the same way, successive layers, taking care not to tamp the latter too much as by so doing the filtration will be very slow and will require excessive suction to get the solution through the filter at all. When the layers have attained a total thickness of about an inch and one-half the whole filter is saturated several times with 1 : 1 HCl to shrink it tighter;

it is tamped some more, and then washed ten times with distilled water. The glass filter \* tube in which the filter is made is shown in photo No. 15. The filter being now ready is transferred, rubber stopper and all, to the bottle in which the solution to be filtered is to be kept.

The photo shows a glass filter tube, but usually a carbon filter tube is too small for filtering the whole solution so that the filter layer is prepared on the porcelain plate supported in a large funnel that pierces a rubber stopper that will fit the neck both of the side neck suction flask shown and of the large glass stoppered bottle in which the filtered solution is to be preserved. The double chloride is then filtered into the latter bottle with moderate suction; kept stoppered; and, to prevent dust from settling around the stopper, a cap of stout paper is tied over the same. The photo No. 15 shows the brass water pump used which

is extremely satisfactory and inexpensive. It discharges into a deep stone box as shown. Cut A illustrates the details of the brass pump.

#### SOLUTION OF THE CHIPS AND FILTERING OUT OF THE CARBON.

Dissolve from 1 to 5 grams of the chips in 60 c.c. of the double chloride per gram of sample in a beaker that has been cleaned from all lint or dust. The chips must be stirred at intervals with a glass rod until there no longer remains on the bottom of the beaker any particles of copper coated steel. The reactions occurring are given herewith for the benefit of the student: In the first place the iron is dissolved away from the carbon by reaction (1),  $\text{Fe} + \text{CuCl}_2 = \text{FeCl}_2 + \text{Cu}$ ; then a further portion of the copper chloride in the double chloride

\* The filter tube shown in photo No. 15 contains a rubber gasket and alundum thimble; these are removed and a perforated porcelain plate is substituted for the carbon filtration.



A

solution causes the metallic copper formed to pass into solution in the manner shown in reaction (2),  $\text{CuCl}_2 + \text{Cu} = 2\text{CuCl}$ . This cuprous chloride ( $\text{CuCl}$ ) would form and separate out as a white precipitate were it not for the excess of acid present in the double chloride which excess of  $\text{HCl}$  dissolves the cuprous chloride; hence it is best to wash the carbon residue on the asbestos filter at first with some of the double chloride before washing it with water.

The carbon is filtered on an asbestos filter supported on a perforated porcelain plate just large enough to fit in a glass carbon filter tube of  $1\frac{1}{2}$  inches diameter. This filter is prepared in exactly the same way as described for the larger filter used for the double chloride. A row of four of these carbon filter tubes are shown in photo No. 15. The well tamped and acid shrunken layer of asbestos need not be over  $\frac{1}{2}$  inch thick. The dissolved chips are poured through the asbestos filter and any black particles of carbon adhering to the walls of the beaker are best discovered by holding the latter over a sheet of white paper. These particles are transferred to the filter by rubbing them loose with a rubber capped glass rod, rinsing the beaker with a fine jet of water and also some of the double chloride. The carbon being now all on the asbestos it is washed five times with some of the double chloride, drawing off each washing with mild suction. The acid is then carefully removed by giving the filter thirty washings, drawing off each one entirely before the next washing is applied. The carbon filter tube is then withdrawn from the rubber stopper. The porcelain plate with its adhering asbestos and carbon is carefully pushed out of the filter tube on to a clean watch glass, with the plate side down. Any carbon sticking to the walls of the filter tube is completely removed by wiping them off with some of the asbestos. The top part of the asbestos filter is first stripped off and placed in the clay combustion boat. This leaves all of the rest of the filter to be used in cleaning out the filter tube. This portion of the filter is now moistened with water. A pair of steel forceps that are not too stiff are used to

hold the portions of the dampened filter that are used for removing carbon that sticks to the filter tube. Then, at the last, the points of the forceps should be wiped off with a little of the pulp as some of the carbon is likely to be on the forceps. The operator should wash his hands before beginning the transfer of the carbon filter and the cleanings to the clay boat. A piece of stout wire or a glass rod is used for pushing the plate and the adhering filter out of the filter tube. Dry the contents of the boat in a water or air oven for two or three hours. When dry, as shown by there being no noticeable condensation upon a cold watch glass placed over the boat immediately after the latter has been taken hot from the air bath, the contents of the boat are pressed firmly down into it and four grams of red lead are spread over the same. The boat is then placed in the electric furnace and the carbon is finished in the same manner as given for the direct combustion. Prior to the burning, the water should not be dried out of the residue in the boat at a temperature exceeding 100° C. The blank is run by placing the same amount of the double chloride in a beaker; filtering it through a filter made as in an actual sample and putting this filter through all of the operations just described, including the red lead covering.

## CHAPTER XI.

### PART V.

#### GRAPHITE IN IRON AND GRAPHITIC CARBON IN STEEL.

IN steels dissolve 3 or 4 grams of drillings in 60 c.c. of 1.20 nitric acid, boil slowly, avoiding the concentration of the nitric acid by adding a little water if necessary, until the flakes of combined carbon are dissolved. Perfectly annealed steel in which graphitic carbon is most frequently found, does not show this flake and the heating is continued until the main solution no longer continues to grow any clearer. This requires about ten minutes boiling.

In pig iron 1 gram is dissolved in 20 c.c. of the above acid aided with 2 or 3 drops of HFl, boiling 10 minutes. The insoluble matter is filtered on the same kind of an asbestos filter as is described for carbon in steel where the chips are dissolved in the double chloride of potassium and copper.

The residue on the filter is washed thirty or forty times with water to remove the iron; then with 1.1 specific gravity KOH solution which is made by dissolving 30 grams of KOH in 200 c.c. of water. The washing with the KOH is continued until the washings are no longer colored brown. Then wash with water as many times as before; then with 1 : 1 HCl to neutralize any remaining KOH; and finally again, thoroughly, with water. The graphitic residue is removed from the filter, dried, covered with red lead, and finished as described in the direct method for carbon in steel, in the electric furnace.

The filtrate from the carbon or graphite, in this method, or in the double chloride method, should be poured through a filter paper and washed free of color to note if any black stain remains on the filter; if there be such a stain then some of the carbon or graphite, as the case may be, has run through and the result will be too low.

## CHAPTER XII.

### PART I.

#### CARBON BY COLOR.

THE determination of carbon by color methods should be indulged in as little as possible. Numerous interferences render analysis, unless carried out under the guidance of persons of long experience, highly inaccurate. The heat treatment, i.e., the greater or less amount of *incidental* annealing that a sample may have had, will cause the color to vary, yielding results from 10 per cent to 20 per cent away from the actual carbon. The perfectly annealed steel, i.e., where the carbon has all been converted into the absolutely annealed condition, yields the greatest depth of color for a given percentage. A few tenths of a per cent of highly coloring elements like chromium give low results compared with a standard steel not containing the alloy. Also the presence of considerable manganese tends to lighten the color in unannealed steel. The same is true of nickel.

If a sample consisting of large, bulky, thick drillings be compared with a standard of small, uniform size, thin drillings, the bulky sample will yield results often 10 per cent too low. The presence of graphitic carbon will cause results to be anywhere from 5 per cent to 90 per cent too low. Of course, much graphitic carbon is easily detected by the insoluble black residue that remains in the solution so that only 5 per cent too low is likely to be unnoticed. A practiced eye will detect the slightest trace of it. If the operator can drill his own samples and always get them with the same heat treatment, and have a standard that has undergone the same treatment, and has been drilled with the same depth of cut, his results will be fairly accurate.

There are two means by which one may approach the ideal:

First. When the drillings to be tested and the standard drillings have been taken from the raw cast steel that has never been reheated and is always allowed to cool slowly from the molten state, i.e., without any quenching.\*

Second. Where the operator is furnished the steel and can anneal it to the last degree of softness, avoiding the temperature range most favorable to the formation of graphitic carbon (see Annealing of Steel). Then drill such samples to uniform thickness and compare them with a standard prepared in exactly the same manner. This second scheme is the most accurate of all color methods. For the identification of the perfectly annealed condition, see Annealing.

Further, it is essential in color work that the standard shall be within 10 per cent of the carbon content of the sample to be tested. The nearer the carbon of the standard is to that of the test, the better; especially is this true of unannealed steel.

*Method.* Dissolve 100 mgs. of sample in 4 c.c. of 1.20 nitric acid. Use a test tube 152 mm. by 15 to 16 mm. diameter. Insist that the dealer supply test tubes that keep within the same diameter. If one test tube is wide and its mate narrow, the wide one will permit more of the free acid to escape than the narrow one, causing variation in the color. Do not set the tubes deep in the boiling water, as it will cause iron to dry on the sides, and, when this is redissolved by shaking the hot acid solution the brown basic nitrate of iron will go into solution, causing another variation of color.† The fewer tests dissolved at one time the better, as some parts of the bath will be hotter than others, causing more loss of acid from the tubes in the hotter location. In forty minutes all of the flakes of carbon are usually dissolved on a water bath. These baths are designed especially for this work, and contain racks to hold thirty-six tubes. These racks have false bottoms perforated with many small holes. This arrangement permits the tubes to be

\* Quenching can be safely done provided the test piece is first cooled to a black heat in an entirely dark closet.

† Some laboratories use glass marbles that rest on the top of the test tubes during the boiling to reduce the evaporation of the acid.

immersed to the depth of 28 mm., which is about the level of the nitric acid.

For more rapid solution of the carbon, requiring from four to seven minutes, use a sand or graphite bath heated to about 190° C. Plunge the tubes into the bath just to the top level of the acid in them. Keep the tubes close together and do not run more than six tubes at a time, as such a bath is liable to great variation in temperature. The writer collects a set of six tubes in a compact cluster and covers all with a 5-ounce beaker. This prevents too rapid loss of acid. Remove the tests the second that the brown flakes are in solution. Use standards within 5 "points" (0.05 per cent carbon) of the tests so that tests and standards will go into solution at about the same moment.

The tests are quickly cooled in running water and compared in the bent-end comparison tubes, which permit the contents of the tubes to be mixed by a rocking motion. The comparison tubes are of 14 c.c. capacity, and graduated to tenths of a c.c. The length of the graduated portion is 181 mm. Then follows 45 mm. of ungraduated tube; then the part bent at an obtuse angle. The bent limb is about 50 mm. long. The outside diameter of the tube is 12 mm. A set of three of these tubes is used. The specifications for these tubes should require that all three tubes be the same inside and outside diameter throughout their graduated portion. The figures and graduation lines should be small, the figures not over 2 mm. long and the lines not over 4 mm. long for c.c., and not over  $1\frac{1}{2}$  mm. long for tenths of a cubic centimeter.

The graduations of all three tubes should coincide with each other. For example, the 14 c.c. mark should be exactly the same distance from the bottom of the comparison tube in each tube of a set, thus proving that the inside diameter is uniform throughout the set.

The tubes should be free of fine black lines due to bubbles in the glass when it was drawn into tubing.

The tubes should be made of selected tubing free of scratches. The graduations should be as exact as those of a burette.

All color carbons should be made in duplicate and results averaged. Nothing is gained by operating on a greater amount than 0.100 gram. The writer, in his practice, ran a great many color tests, using 0.500 gram, and found the same lack of agreement, and much more acid is needed.

*The Comparison.* If, for example, a 0.60 carbon standard is in use pour it into the comparison tube, using as little rinse water as possible, so that the volume of the fluid in the tube is just 6 c.c.; mix thoroughly.

The test is then put in another tube, and water is added to it until its color is the same shade as that of the standard, mixing carefully with each addition of water. This matching should be conducted slowly when the test is still but slightly darker than the standard. But two-tenths of a cubic centimeter should be added at a time when the test is only slightly darker than the standard, so that when the former is finally very slightly lighter than the standard, the operator knows he has overstepped the end point 0.01 per cent, which he deducts from the reading. If the test, for example, is just turned lighter at 6.5 c.c., then the per cent carbon will be 0.65 less 0.01 or 0.64 per cent carbon. If a standard of 0.30 carbon is in use, it is diluted to 9.0 c.c. Should the test match it at 6.0 c.c., then the carbon percentage will be  $0.60 \div 3$ , or 0.20 per cent carbon. If a standard of 0.40 carbon is used, it is diluted to 8.0 c.c. If the test matches it at 7.0 c.c. for example, then the per cent carbon will be  $0.70 \div 2$ , or 0.35 per cent carbon. If a standard of 0.08 per cent carbon is in use, it is diluted to 5.6 c.c. Should the test match it at 6.0 c.c., for example, the per cent carbon would be  $0.60 \div 7$ , or 0.085 = per cent carbon. When a large number of color tests must be made, they should be checked at frequent intervals by combustion; for instance, if a lot of 30 color tests are made, and every fifth one is checked by combustion and checks within 0.01 to 0.03 per cent in a range from 0.50 per cent and over, it is pretty safe to assume that that particular lot of color tests was done under favorable conditions.

The writer does not use a comparison camera, but decidedly

prefers to hold the tubes on a sheet of white paper in diffused sunlight. The direct glare of the sun is, of course, undesirable.

At night a 50-candle power frosted electric lamp of filament type resting on a sheet of white paper from a flexible arm is the best source of light. The comparison tubes should be held\* with the graduations touching each other, thus giving a clear field of color. Their relative right and left positions should be changed at intervals of a few seconds to assist the operator in judging respective depths of color. He should endeavor to lose track of which is test and which is standard, and if, under such conditions, he finds he can come to the same conclusion three times in succession, then he is as certain as possible of his choice of the light one and the dark one. In the writer's opinion the least source of error in carbon color work is the operator's eye. A man with a good eye for color and plenty of practice can be counted on not to introduce an error due to the eye of over 0.02 per cent in higher carbons and of not over 0.010 per cent in lower carbons, around 0.08 and perhaps not over 0.005 per cent in the latter range.

Reject all drillings that are blued, or rusty.

\* The comparison tubes should be held at an angle of about 45 degrees to the paper with their ends touching the same.

## CHAPTER XII.

### PART II.

#### VOLUMETRIC PHOSPHORUS IN PIG IRON, STEEL, WASHED METAL AND MUCK BAR.\*

DISSOLVE 1.63 grams of sample in 45 c.c. 1.13 nitric acid, using a 5 ounce beaker. Heat gently on hot plate or bath of some description. The writer uses a twelve-hole affair as shown in Fig. 16. Highly silicious pig iron dissolves slowly and it is best to maintain all pig iron samples at digesting heat (barely boiling) for at least twenty minutes. To assist in dissolving pig iron add four drops of hydrofluoric acid to the solution after it has been digested ten minutes with the nitric acid, if high silicon is suspected.

For pig iron and some chrome steels the next step is to filter out the insoluble graphite, etc. Wash the residue on the filter fifteen times with the dilute nitric acid wash. All phosphorus filtrations in this laboratory are made on a revolving filter stand. (See Fig. 17.)

It is not necessary to filter solutions in plain carbon steels. Filter the muck bar solutions if they contain much insoluble residue.

Add to the filtered solutions of pig iron, chrome steel and muck iron and to the unfiltered solutions of plain steel and washed metal, from a convenient drop bottle, the potassium permanganate solution. Continue the addition of permanganate until the excess of manganese separates as a brown precipitate that does not disappear noticeably after 10 minutes boiling. As washed metal usually contains about 3.00 per cent of carbon it will consume considerably more of the permanganate.

\* Hundeshagen (modified by J. O. Handy) first recommended the titration of the yellow precipitate by standard alkali.

ganate solution before the carbon is destroyed than ordinary steel. The excess of manganese precipitate is removed by adding ferrous sulphate solution, free of phosphorus, from a dropper until the solution is again clear. After five minutes more boiling the beakers are removed from the fire, the covers are rinsed off and the inside walls of the beakers are washed

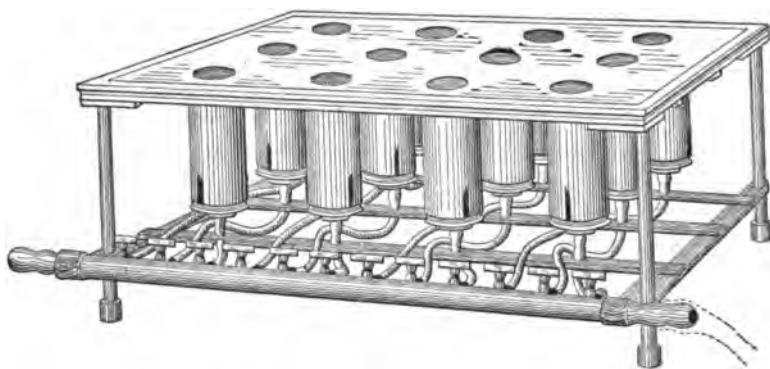
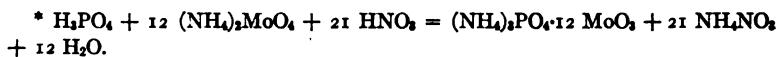


FIG. 16.  
Phosphorus in steel.

(to prevent the phospho-molybdate sticking to the walls) down, and 50 c.c. of the ammonium-molybdate\* are run into each test from a measuring siphon. (See Fig. 18.) A batch of 12 tests are stirred at a time, using glass rods. A single test is stirred around twice, then the next one, and so on until each test in the lot has been stirred ten times. This means that each solution has been stirred at intervals during a period of ten minutes. The twelve samples are put on the revolving stand and twelve 7 cm. filters are marked with a lead pencil to correspond to the respective tests. The only interval between the completion of the stirring and commencement of the filtration is the time required to fit the filter papers to the funnels.

The liquid is decanted through its proper filter and the bulk of the precipitate is allowed to remain in the beaker until the



filter papers are washed ten times, giving each paper a washing, then the next one and so on until number one is reached again. By the time number one is ready for its second washing, the first washing will be well drained off. Each funnel stem is given a turn with the thumb and forefinger in such a manner

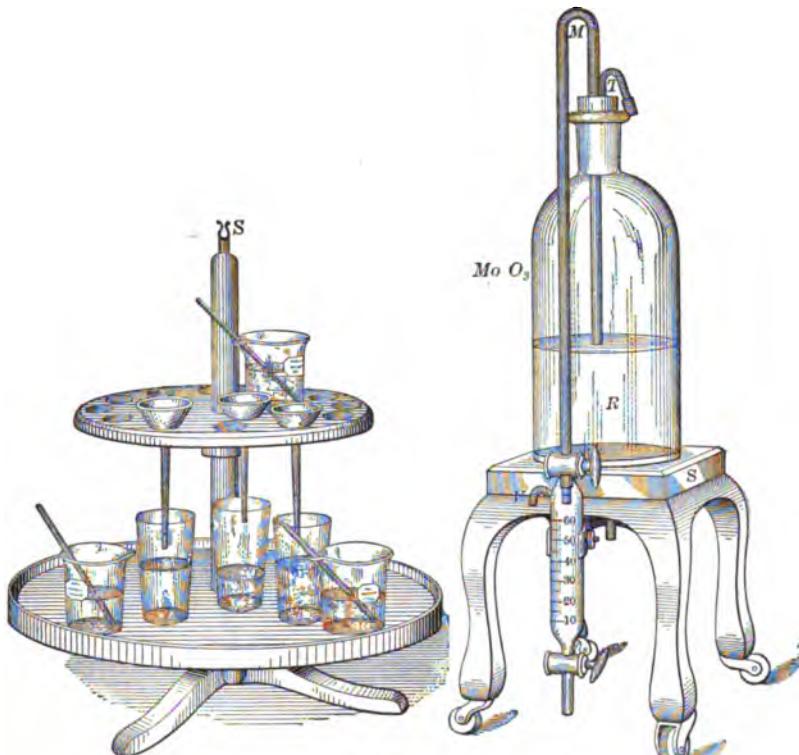


FIG. 17.  
Phosphorus in steel.

FIG. 18.  
Phosphorus in steel.

that the double fold of the paper is washed twice and the single fold once during each washing. Use the dilute nitric acid wash.

Ten washings having been accomplished, the main body of the yellow precipitate is washed on to its respective filter with a fine jet of the acid wash, and receives a further ten washings to remove iron.

To remove free acid the precipitates are next washed thirty times with the potassium nitrate water. The filters are now removed to a large watch glass. A ruled slip is dated and headed and the various tests are entered thereon. On the right-hand side is kept a record of the alkali used, and on the left, the acid standard used in the subsequent titration of the yellow precipitate.

The titration is accomplished by placing filter and precipitate in a 100 c.c. beaker. The standard sodium hydroxide solution, 1 c.c. of which equals 0.01 per cent phosphorus when 1.63 grams are taken, is dropped on the filter until the yellow precipitate has\* dissolved.† Then add 50 c.c. distilled water. Two drops of phenolphthaleine are introduced, and from a second 50 c.c. burette standard nitric acid is run into the rose colored solution until one drop of acid discharges this color. The total number of c.c. of alkali added, less the number of c.c. of acid required to discharge the rose color, multiplied by 0.01, gives the percentage of phosphorus in the sample.‡

#### GRAVIMETRIC PHOSPHORUS.

If it is desired to check the volumetric method by weighing the yellow precipitate, proceed exactly as given under the latter process, with the following exceptions:

First. Filter *all* solutions as in pig iron.  
Second. Omit the washing with potassium nitrate and use only the dilute nitric wash to remove iron, leaving the acid in the filter paper.

Third. Filter the yellow precipitate on 7 cm. ashless filters that have been previously weighed hot between watch glasses with edges ground to fit water-tight when held firmly together, nearly full of water, in a vertical position.

\* The following equation explains how the solution takes place:  $(\text{NH}_4)_2\text{PO}_4 \cdot 12\text{MoO}_3 + 24\text{NaOH} = (\text{NH}_4)_2\text{PO}_4 + 12\text{Na}_2\text{MoO}_4 + 12\text{H}_2\text{O}$ .

† It is safer to add, at least, 1 or 2 c.c. excess of the alkali standard.

‡ Figs. 16, 17 and 18 were designed some years ago by Dr. Edward S. Johnson.

These filters are weighed as rapidly as possible after having been dried at the temperature of boiling water. The phosphomolybdate is collected on the weighed filters and washed free from iron with the dilute nitric acid. The filters are again dried as before, for one hour, and weighed. The weight of the filter paper plus the dried precipitate, less the weight of the paper, less the blank (obtained by filtering a clear filtrate from some previous phosphorus determination through a weighed paper, washing it, drying it and reweighing it as in an actual analysis) equals the percentage in the sample when 1.63 grams are used for analysis. This method is valuable only as a check, as too much time is consumed.

In both methods the filtrates and washings are placed on a shelf for one hour. If a cloudy ring forms at the junction of the washings and the main body of the filtrate, results will be too low. If the cloud gradually spreads, the results may be as much too low as 0.01 per cent in a possible 0.100 per cent.

After considerable practice one can estimate with sufficient accuracy for most mill control all phosphorus 0.02 per cent and under by simply examining the yellow precipitate after it has had an opportunity to settle for about twenty minutes in the 5-ounce beaker. The prevention of cloudy filtrates will be discussed under the heading "*Molybdate Solution.*"

#### STANDARD SODIUM HYDROXIDE SOLUTION.

One hundred and fifty grams of sodium hydroxide and one gram of barium hydroxide are dissolved in 1000 c.c. of water. Let the solution stand for two days. Siphon off the fluid and dilute it to two liters. Dilute 275 c.c. of this stock solution to 3500 c.c. On testing, suppose it is found that 20 c.c. of the alkali standard equal 20.75 c.c. of the acid standard. This gives the proportion  $20 : 20.75 :: 3400 : x$  ( $= 3527$ ). Therefore dilute the remaining 3400 c.c. to 3527 c.c. when 20 c.c. of the NaOH standard will equal 20 c.c. of the standard acid or 1 c.c. NaOH = 0.010 per cent phosphorus when 1.63 grams of

sample are used for analysis. It is always best to confirm this value by running several steels whose phosphorus content is accurately known.

#### STANDARD NITRIC ACID.

Dilute 74 c.c. 1.20 nitric acid to 3500 c.c. On titrating with standard NaOH, suppose it is found that 19.2 c.c. of the acid equal 20 c.c. of the alkali : 19.2 c.c. : 20 c.c. :: 3400 :  $x$  ( $= 3541$ ).

Therefore the remaining 3400 c.c. are diluted to 3541 c.c. when 20 c.c. of standard acid should equal 20 c.c. of standard alkali.

For preparation of 1.20 specific gravity nitric acid from concentrated acid see Chapter XX.

#### MOLYBDATE SOLUTION.

Dissolve 183 grams of unignited molybdic acid plus 2 grams of ignited (melted) molybdic acid in 900 c.c. of 11.50 per cent ammonia water plus 250 c.c. of distilled water. Cool this solution and add it a little at a time to 2700 c.c. 1.20 nitric acid. Cool the nitric acid after each addition of the molybdate. If the nitric acid is allowed to get too greatly heated the molybdic salt will precipitate in large quantity. Filter through a pulp filter (using suction) after twelve hours' standing.

Some years ago the writer observed that a solution of ammonium molybdate in nitric acid, made as here given, will produce different varieties of the yellow precipitate. Other conditions being unchanged, an ammonia solution of molybdic acid prepared from ignited, i.e., crystalline anhydrous molybdic acid, causes the yellow precipitate to separate from the nitric acid solution of the steel in an extremely fine state of division. Such a precipitate will remain suspended in the solution for hours without subsiding and will run through a filter paper almost as though it were a solution instead of a precipitate. This precipitate has only one redeeming feature: It is the least soluble in the dilute nitric wash of any of the varieties of ammonium phospho-molybdate that are encountered under the conditions that are cited here. Now if no ignited molybdic acid

is used in the preparation of the molybdate solution, the phospho-molybdate settles rapidly and does not run through a filter. But this variety has the objection that it is the most soluble form of phospho-molybdate, in nitric acid. This variety of precipitate will leave the filtrate perfectly clear, but after the latter has stood for an hour (if much precipitate has dissolved in the wash water) or perhaps not until the next day (if little of the yellow precipitate has dissolved in the dilute nitric wash) a milky ring of phospho-molybdate will appear at about the point where the washings lie on top of the main body of the filtrate. If much of the yellow precipitate has been dissolved, say about  $\frac{1}{10}$  or  $\frac{1}{20}$  of its weight, this cloud will spread through the entire filtrate.

The ideal yellow precipitate is that one whose physical condition is such that it will give a clear filtrate and be practically insoluble in the wash. The author has had brands of molybdic acid that require equal weights of the crystalline molybdic acid and of the unignited variety to produce the desired results. At present but 2 grams of the crystalline material are needed for the particular brand of molybdic acid now in use.

To prepare crystalline molybdic acid the author melts in a porcelain dish the ammonia-free, so-called c.p., molybdic acid which melts rapidly at a bright red heat to a clear fluid, and, on cooling, forms handsome crystals that can be readily reduced to a powder in a porcelain mortar.

#### POTASSIUM PERMANGANATE SOLUTION FOR OXIDATION OF THE CARBON.

Fifty grams of the salt dissolved in one liter of water.

#### FERROUS SULPHATE SOLUTION.

Two hundred and fifty grams of the phosphorus-free salt dissolved in 1000 c.c. of water acidulated with 20 c.c. 1 : 3 sulphuric acid.

**DILUTE NITRIC ACID WASH.**

Two hundred and thirty c.c. 1.20 nitric acid diluted with 8100 c.c. of water.

**POTASSIUM NITRATE WASH.**

Dissolve 50 grams of potassium nitrate in 2500 c.c. of water for a stock solution.

Dilute 700 c.c. of the latter with 7000 c.c. of water to constitute the wash.

**PHENOLPHTHALEINE INDICATOR.**

One gram of this substance is dissolved in 100 c.c. of absolute alcohol.\*

**PHOSPHORUS IN VANADIUM STEEL.**

E. W. Hagmaier, in Met. Chem. Eng., Vol. XI, No. 1, separates the phosphorus by cerium chloride. In the case of a tungsten steel, dissolve the steel as for tungsten as given on pages 98 to 100. Instead of adding the molybdate solution as directed on page 100, this chloride solution should be entirely reduced with  $\text{SO}_2$ ; then add 5 c.c. of 90 per cent acetic acid and 10 c.c. of a saturated solution of cerium chloride. Next add 1 : 3 ammonia slowly until a permanent turbidity is obtained. Boil; let settle; filter; wash a few times with hot water; dissolve in 1 : 1 hot nitric acid and precipitate the phosphorus with molybdate solution. If the vanadium is in excess of 1 per cent, the cerium phosphate must be redissolved, and reprecipitated to remove all of the vanadium. The cerium phosphate is then dissolved off the filter with the nitric acid and finished as above.

\* See remarks at the close of Chapter XI, page 218, on the proper way to drill a steel sample in order to obtain borings that represent the average of the piece in phosphorus, sulphur, silicon and carbon.

## CHAPTER XII.

### PART III.

#### THE ANALYSIS OF FERRO-PHOSPHORUS.

##### SILICON.

FUSE 0.5 or 0.6 gram of the floured sample in a finely ground mixture of 10 grams of sodium carbonate and 2 grams of potassium nitrate in a platinum crucible. After a complete fusion is gotten as shown by the melt being practically free of boiling at a bright red heat, cool the melt by running it around the sides of the crucible; dissolve it out of the crucible with water in a platinum dish; transfer the water solution and all to a 600 c.c. casserole, cleaning the crucible by heating in it some conc. HCl; add the cleanings to the casserole whose contents have been meanwhile acidulated with 75 c.c. of conc. HCl. Heat the casserole with a watch glass on it until all effervescence has ceased; remove the cover and evaporate to dryness; cool; add 20 c.c. of conc. HCl; heat for some minutes to dissolve the iron; add 150 c.c. of water and heat again to dissolve the sodium salts; filter out the silicic acid and wash it free of iron test with 1 : 20 HCl. Burn off the paper containing the silicious matter in a weighed platinum crucible and finish it as in steels, using HF and a few drops of H<sub>2</sub>SO<sub>4</sub>. (See page 286.) The residue remaining after volatilizing the silicon may contain a little iron and phosphorus. Fuse this residue with 20 times its weight of anhydrous sodium carbonate; dissolve the fusion with HCl and add the solution to the main filtrate from the silicious matter.

##### PHOSPHORUS.

The main filtrate from the silicon now contains all of the phosphorus and iron. Dilute this filtrate to 400 c.c. with water; add 2 grams of citric acid, to keep the iron from reprecipitating,

and then a slight excess of ammonia. Heat the solution to nearly boiling and pass through it a stream of hydrogen sulphide that has been washed by bubbling through a wash bottle containing about an inch of distilled water. The original form of the 2 quart Kipp is the most practical form of  $H_2S$  generator. The iron sulphide that is supplied fused and in sticks is the best for this work. The 1 : 1 HCl should be used to attack the iron sulphide. When the black sulphide in the main filtrate has settled out well and falls to the bottom of the beaker, stop the stream of the  $H_2S$  and filter out the sulphides of iron and some platinum (the crucible is attacked some by the niter in the flux). Wash the sulphides about fifteen times with water saturated with  $H_2S$ . Place the filter containing the sulphides in a porcelain dish and pour over it 30 c.c. of 1 : 1 HCl and warm it with the cover on at not over a water bath temperature for an hour to dissolve the iron sulphides. If platinum is present there will remain some insoluble platinum sulphide which can be filtered out together with the paper pulp from the first filter which was placed in the acid. The second filter is washed at least twenty times with 1 : 40 HCl and then further until the washings no longer give an iron test with either potassium ferricyanide or with ammonium sulphocyanate. This filtrate and washings from the pulp and platinum sulphide contain all of the iron and perhaps still a portion of the phosphorus. 2 grams of citric acid are again added and the iron is again separated in hot solution with  $H_2S$  as before. Filter out the sulphide of iron and wash it as in the first instance. Retain the iron sulphide to get the total iron. The two sets of filtrates and washings from the  $H_2S$  precipitations are combined and made acid with about 50 c.c. of 1 : 1 HCl and are heated with a cover on until all effervescence due to the escape of  $H_2S$  is over. Remove the cover and evaporate to 100 c.c.; add water if necessary to dissolve any crystals that may have formed; filter out any insoluble matter; add 150 c.c. of conc. nitric acid and heat in the covered beaker until all action between the nitric acid, the chlorides, and the citric acid is over; then transfer to a large casserole and evaporate

low. When brown fumes begin to develop again, cover the vessel and add 50 c.c. more of the conc.  $\text{HNO}_3$ . Heat until all action is over; remove the cover and evaporate to dryness; cool; add 75 c.c. of conc.  $\text{HCl}$ ; cover; heat until action ceases; evaporate again to dryness; cover again; add once more 75 c.c. of  $\text{HCl}$  and evaporate dry; cool; heat with 25 c.c. of conc.  $\text{HCl}$  with the cover on for 10 minutes; add 150 c.c. of water to dissolve the salts; filter; wash the filter with water until the washings are free of chlorides; make the filtrate and washings just neutral with ammonia; cool; add 40 c.c. of magnesia mixture; stir well; add to the solution one-third of its volume of conc. ammonia; and stir the solution for one or two minutes and let it stand for 12 hours. Then filter out the ammonium magnesium phosphate and wash it with 5 c.c. of conc. ammonia diluted with 500 c.c. of water, until the washings no longer give a cloudiness after being acidulated with a few drops of dilute nitric acid and tested with a little silver nitrate solution. The washings should be kept separate from the main filtrate. Both the filtrate and washings should be tested by adding 10 c.c. more of the magnesia mixture and to the washings should be also added one-third of its volume of ammonia. If any precipitate forms in either the filtrate or the washings it is filtered, washed and added to the main precipitate. Dry the filters containing the phosphate precipitates, and then smoke off the volatile portion of the filter papers below redness to avoid losing particles of the phosphate; do not heat the platinum crucible hot enough to ignite the gases coming from the papers. When the smoking ceases, raise the heat to low redness, and finally hot enough to obtain a pure white residue of magnesium pyrophosphate. Do not use a blast lamp temperature as the platinum will be badly attacked by the phosphate. Weigh the  $\text{Mg}_2\text{P}_2\text{O}_7$ ; dissolve it in  $\text{HCl}$ ; filter out any insoluble silica; wash it; weigh it and deduct it from the first weight; calculate the net weight to metallic phosphorus by use of the factor 0.2787.

*Magnesia Mixture* consists of 25 grams of magnesium chloride, 50 grams of ammonium chloride, 100 c.c. of conc. ammonia

and 200 c.c. of water. This mixture is stirred until the salts are dissolved, and after standing for at least 24 hours it is filtered for use.

*Sulphur* in ferro-phosphorus is obtained by fusing the finely ground sample as given for phosphorus, continuing the analysis exactly as for this element until the silicon has been filtered off. The filtrate and washings from the silicious matter are then diluted to 400 c.c. and the sulphur is precipitated with  $\text{BaCl}_2$  using 25 c.c. of a saturated solution of the barium salt. The barium sulphate is filtered off after 12 hours and the determination is then finished as in steels.

*Iron* is obtained from the sulphide gotten from the second precipitation with  $\text{H}_2\text{S}$  in the analysis for phosphorus. The sulphide is roasted in a porcelain crucible until free of the paper; the ash is dissolved in HCl; reduced with stannous chloride and titrated with potassium dichromate as in iron ore. The iron can also be obtained in the sulphur determination by fusing 1 gram of the sample as above for sulphur; the filtrate from the silicious matter can be divided into two equal parts and one part can be finished for sulphur and the other half is precipitated with ammonia to remove the platinum from the iron. The latter is then dissolved off the filter with HCl and finished as given for iron ore.

*Manganese* is gotten in the same manner as for manganese in insoluble ferro-titanium. (See page 52.)

#### TYPICAL ANALYSES.

	No. 1.	No. 2.
Iron.....	79.44	78.16
Manganese.....	0.05	0.06
Phosphorus.....	18.51	20.45
Sulphur.....	0.67	0.55
Silicon.....	0.76	0.54
Carbon.....	0.26	0.16

## CHAPTER XII.

### PART IV.

#### SULPHUR IN STEEL, MUCK BAR, PIG IRON AND WASHED METAL.

##### VOLUMETRIC.

DISSOLVE three grams of sample in 70 c.c. of 1 : 1\* hydrochloric acid. More than this amount of acid is sometimes required for rapid solution. The dissolving flask is the author's design and is made in a mold with a fire finish, ring neck. The flask, being made in a mold instead of by hand, has a perfectly round neck and always takes a No. 6 rubber stopper. Its capacity is 275 c.c. to base of neck, and its height is 165 mm. It is a great convenience to have these details always the same. (Fig. 4.) Previous to designing this flask much trouble was experienced in different lots of flasks. In the same lot some would require a No. 4, others a No. 5, and some a No. 6 stopper to get a good fit. Then ground finish flasks will crack at the neck when placed in the heater to dry out the water. Drillings are never weighed into wet flasks. The No. 6 stopper is perforated with three holes, one to receive a bulb funnel of 75 c.c. capacity. This funnel is also designed to facilitate the work. It has an opening at the top of the bulb of 15 mm. diameter. The glass cock has an extra large hole bored in it ( $3\frac{1}{2}$  mm. diameter) to

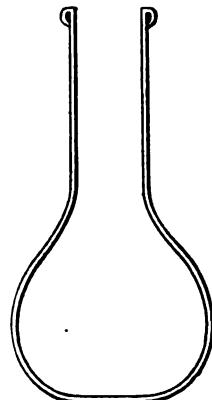


FIG. 19.

\* 2 parts of 1.20 HCl (conc.) to 1 part of water are more reliable as some kinds of pig iron show no sulphur at all by the evolution method with weaker acid.

permit of rapid flow of the acid from the bulb into the flask. The total distance from the base of the bulb to the outlet in the stem is 145 mm. The second hole in the stopper admits a small tube that dips just below the level of the fluid in flask. After the iron is completely dissolved, hydrogen is forced through this inlet for from three to five minutes to drive out any hydrogen sulphide that may remain in the interior of the flask. The third hole admits the delivery tube which carries the evolved gases to the bottom of the absorbing solution of ammoniacal cadmium chloride. This solution is contained in a thick wall, thick bottom, test tube about 10 inches by 1 inch. Fifty c.c. of the solution are used for each analysis.

The flask is clamped in a rack supporting four flasks to the stand.\* Each stand is supplied with four burners. The top of the stand on which the bottoms of the flasks rest is an asbestos copper-rimmed board with a circular hole of 42 mm. diameter cut in it immediately over each burner. The bottom of the flask rests in this hole. Ranged alongside of this rack is a wooden one holding the four absorption tubes. As many such sets of four are in operation at one time as the chemist can manage.\*

When the solutions no longer evolve gas to any extent without the aid of heat, the flames are raised slightly so as to maintain a very slight boiling action. When heat no longer produces gas bubbles in the absorption tubes, the hydrogen is turned in and a rather rapid passage of this gas is continued for from three to five minutes. The cocks on all of the bulb funnels are then opened. The hydrogen is shut off at each flask.

The cadmium solution containing the precipitate of sulphide is poured on a rapid running No. 597, 11 cm. S. & S. filter. The absorption tube is rinsed with water and the washings are poured on the filter. The latter is washed three or four times with water. The delivery tube, if much precipitate adheres to it, is cleansed by rubbing it with a little filter paper. This small piece of paper is then dropped in on the main portion of the cadmium sulphide to which it belongs. The delivery tube

\* See Fig. 2, page 104.

without further washing is put back into its respective absorption tube.

Both tubes together with the filter paper containing the major part of the sulphide are taken to the titration table together with the other tests which have been similarly prepared. The filter paper with the adhering sulphide is placed in a 1000 c.c. beaker containing 500 c.c. of water. For convenience the beaker should have an etched mark on it to indicate the half liter.

The paper is beaten into fragments with a glass rod and the pulp is stirred all through the water. Two c.c. of starch solution are added. The absorption tube corresponding to this filter is filled one-quarter full of distilled water and then to within an inch of the top with 1 : 1 hydrochloric acid. Further, the delivery tube, which has been momentarily removed from the absorption tube previous to adding the water, is returned to the acid fluid, and is raised and lowered in it to dissolve any small quantity of cadmium sulphide adhering to its interior or exterior walls. It is then laid aside and the fluid in the absorption tube is poured into the water containing the bulk of the yellow sulphide. This acid is not dumped in promiscuously but is allowed to run down the inner wall of the beaker rather slowly so as not to disturb the contents thereof. Before stirring the acid through the latter, iodine is dropped in from a Gay-Lussac burette held in the operator's left hand. The drops are added in such a way that a circle of drops extends around the inner circumference of the beaker. With his other hand the operator now gives the solution in the beaker a *slight* stir with a glass rod. If this causes the blue to disappear, leaving a reddish tint, another circle of drops of iodine is added, and so on until two or three drops of the standard iodine solution produce a purplish blue end point which does not fade to a red with more stirring.

The number of c.c. of iodine used less the number of c.c. required to produce a faint blue in a blank test, multiplied by the percentage value in sulphur of the iodine standard, equals

the per cent of sulphur. The blank test is made on the same amounts of starch, filter paper and water as are used in an actual analysis.

This sulphur value is obtained by running steels of known sulphur content in the manner described.

The U. S. Bureau of Standards, Washington, D. C., also furnishes phosphorus, sulphur, silicon and manganese standards for pig iron and steel that have been analyzed by chemists experienced in iron and steel analysis. These constitute a valuable aid to the analyst, enabling him at any time to check his own standards. The cost of these standards is low. Steps are being taken with a view to preparing also a series of various alloy steel standards standardized as to vanadium, titanium, chromium, tungsten and molybdenum content.\*

Each day a standard steel should be run with the other work, as new acids and chemicals are liable to cause the sulphur value of the iodine to change from that originally obtained when it was first standardized.

This method is accurate for all unhardened plain carbon steels, and for annealed pig iron and for muck bar. In chilled pig iron, unless first annealed, the results are usually about 25 per cent lower than the actual sulphur, and yet, in spite of this fact, by reason of its rapidity, practically the method as given is very generally in use by buyer and seller of pig iron. The practice of annealing the drillings in covered crucibles, at a red heat, for 15 minutes, may probably come into vogue.

However, if the buyer and seller understand the limitations of the method it would seem unnecessary to resort to this detail. The steel furnace superintendent could calculate his sulphur content one-fourth higher than the laboratory report. Or the buyer and the seller could agree that if their respective laboratories find 0.060 per cent sulphur, for example, in pig iron, it shall be reported as 0.075 per cent, thus saving valuable time in

\* As is generally known the U. S. Bureau of Standards now has plain vanadium, chrome-vanadium, chrome-nickel, chrome tungsten and plain nickel standards for distribution at a reasonable rate.

the laboratory and yet have records that are sufficiently close to the truth for all practical purposes.

The evolution method is unreliable for steels high in copper and for many alloy steels that form carbides that are insoluble in 1 : 1 hydrochloric acid. The results are too low. (See analysis of these steels.\*)

#### THE STARCH SOLUTION.

Grind 1 gram of good wheat starch, free from rancid smell, to a powder. Stir it with 10 c.c. of water in a small beaker and put it carefully into 90 c.c. of boiling water. Cool and use as needed. It is best to prepare this solution daily.

#### IODINE STANDARD.†

One gram of best resublimed iodine is dissolved in a very little water together with 10 grams of c.p. potassium iodide. This is diluted to 1000 c.c. with distilled water. It is standardized against a steel of known sulphur content.

#### CADMIUM CHLORIDE SOLUTION.

Twenty grams of anhydrous cadmium chloride are dissolved in 1400 c.c. of ammonia water of 0.9 specific gravity. This solution is diluted to 4 liters with distilled water for use.

#### LEAD ACETATE SOLUTION.

For purification of the hydrogen before it enters the sulphur flasks, it is allowed to bubble through a 500 c.c. Bunsen wash bottle containing a solution of lead acetate made as follows:

- (1) Dissolve 100 grams of lead acetate in 400 c.c. of water.
- (2) Dissolve 400 grams of potassium hydroxide in 500 c.c. of water. Pour one solution into the other and mix thoroughly. Use 120 c.c. of this solution in each wash bottle.

The hydrogen is generated in an ordinary Kypp apparatus.

\* Read pages 102 and 104.

† One c.c. of this standard equals from about 0.0042 to 0.0045 per cent of sulphur when 3 grams of sample are taken for analysis.

**GRAVIMETRIC SULPHUR IN PIG IRON, STEEL, WASHED  
METAL AND MUCK BAR.**

Dissolve 5 grams of drillings of 0.04 per cent and higher sulphur content in 200 c.c. concentrated nitric acid, using an 800 c.c. beaker. For percentages of sulphur under 0.04 per cent use 10 grams of drillings, dissolving the latter in 300 c.c. of concentrated nitric acid. Add the nitric acid a few c.c. at a time, as the reaction is violent. When all acid is in the beaker, warm the contents of same until action is over. Then add 2 grams of sodium carbonate. Transfer the solution to a No. 6 dish and evaporate on the sand or graphite bath to dryness. Dissolve in 100 c.c. of 1.20 hydrochloric acid, keeping the dish covered until spraying ceases. Remove the cover and evaporate to dryness again. Dissolve once more with 50 c.c. concentrated HCl and evaporate to a scum. Add 10 c.c. of concentrated hydrochloric acid, or more if necessary, and heat with cover on until all iron is in solution. Add 100 c.c. of water. Filter; wash with dilute HCl (1 : 20). Dilute the filtrate and washings to 400 c.c. Heat to boiling. Add 60 c.c. of a saturated solution of barium chloride, diluted with 200 c.c. of water. Filter the barium chloride before using it. Stir the solution thoroughly after adding the barium chloride. After twelve hours filter the precipitated barium sulphate on a double 9 cm. ashless filter. Barium sulphate is quite soluble, even in very dilute hydrochloric acid. It should be washed free from iron with cold water and only an occasional washing with water containing one or two drops of 1 : 1 hydrochloric acid in 100 c.c. of distilled water.

Wash about every fifth time with this acidulated water until no iron test is obtained with KCNS and then free from chloride test with water alone. Ignite in a weighed platinum crucible. Add one or two drops of 1 : 3 sulphuric acid and ignite again. Weigh as BaSO<sub>4</sub>. Obtain a blank in the same way. Deduct the BaSO<sub>4</sub> found in the blank and multiply the remainder by 13.73 and divide the product by the weight taken

for analysis to obtain per cent of sulphur. If the barium sulphate does not burn white it can be fused with 1 gram of sodium carbonate. The melt is then dissolved in water; filtered from BaCO<sub>3</sub>; the filter washed with water and the filtrate and washings acidulated with a slight excess of 1 : 1 hydrochloric acid. Heat to boiling and precipitate with 10 c.c. of a filtered, saturated solution of barium chloride diluted to 50 c.c. with water. Finish as before, *washing this time with water only.*

## CHAPTER XII.

### PART V.

#### MANGANESE IN PIG IRON, TUNGSTEN STEEL, MUCK BAR, NICKEL STEEL, MOLYBDENUM STEEL, VANADIUM STEEL, TITANIUM STEEL AND CHROME STEEL.

FOR pig iron, muck iron, plain carbon or plain vanadium steel or nickel steel, titanium steel with *absence* of chromium and with silicon not over 1 per cent, and tungsten steel not over 3.5 per cent tungsten, accurate to 2 per cent of manganese. Dissolve 0.100 gram for manganese of not over 1 per cent manganese or 0.050 gram for higher percentages in 40 c.c. 1.20 nitric acid in a 10 by 1 inch test tube over a low Bunsen flame. (See Fig. 20.)

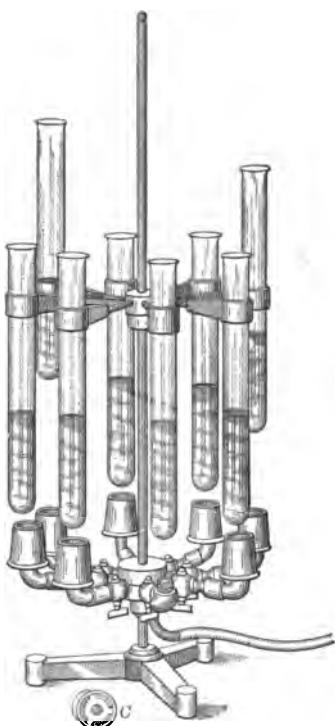


FIG. 20.  
Manganese in steel.

\* Fig. 20 is after a design by Dr. E. S. Johnson.

After adding the lead to all of the tubes, raise the flames causing the contents to boil almost to the top of the test tubes, four minutes. Lower the flames, place the tubes *quickly* in cool water, and then, after a few seconds' delay, directly into cold water. Permit the excess of lead peroxide to settle ten minutes, or longer if convenient, in a dark cupboard.

Decant the contents of the tubes into 5 ounce beakers as needed, leaving all black sediment in the bottom of the test tube. Titrate the pink solution with standard sodium arsenite until all pink or brown shades are gone and a suggestion of yellow color appears. The writer has tried many methods for the quick determination of manganese, and can recommend it in preference to other methods for simplicity, speed and accuracy. Chromium is about the only disturbing element likely to be met with in steels, and can be quickly removed by the following method, which is used also for all high-speed combinations and high per cent tungsten steels:

Dissolve 0.300 gram or 0.150 gram in low and high manganese steels, respectively, and proceed exactly as given for the determination of manganese in chrome-vanadium steels. (See Analysis of Vanadium Steels, page 15.)

For plain molybdenum steels without chromium, proceed as in plain steels. Presence of large quantities of copper and nickel do not interfere with this method. Of course, hydrochloric acid should be absent, or any other substance that would reduce permanganic acid, such as carbonaceous materials. Sunlight bleaches the pink color, causing low results.

For the determination of manganese in cobalt steels, see page 321.

#### STANDARD SODIUM ARSENITE SOLUTION.\*

**Concentrated Stock Solution.** 2.48 grams of c.p. arsenious acid and 12.5 grams of c.p. fused sodium carbonate dissolved in 1250 c.c. of distilled water. Dissolve the arsenious acid and the carbonate, at first, in a little hot water.

\* Deshay suggested the sodium arsenite titration.

**Working Strength.** 200 c.c. of stock solution diluted with 1600 c.c. of water. One c.c. of this solution will equal, usually, 0.07 per cent of manganese when 0.100 gram of sample is taken. It should be checked against steels of known manganese content before it is used.

**THE AUTHOR'S MODIFICATION OF THE PERSULPHATE AND  
LEAD PEROXIDE METHODS FOR MANGANESE IN  
EXCESS OF 2 PER CENT.**

The author has tested the following schemes for manganese up to 15 per cent:

*By lead peroxide:* Dissolve 0.100 gram of the steel in 350 c.c. of 1.20 nitric acid in the style of flask shown on page 269 and of 500 c.c. capacity. Boil the solution on the Argand heater shown on page 258 for 20 minutes, keeping the flask covered with a 1 inch watch glass, and boiling gently. Add a little precipitated silica before starting to boil to prevent uneven boiling. Remove the flask from the fire and add 10 grams of the *light brown* lead peroxide. Put back on the heater and boil quietly for 5 minutes. Cool the flask in running water and permit the lead to settle for *at least 3 hours*. Decant the deep purple supernatent fluid into a 400 c.c. beaker, taking great care not to pour off any of the lead oxide lying in the bottom of the flask. Add to the decanted liquor a standard solution of ferrous ammonium sulphate until all pink and brown tints are gone from the test and the liquid has an almost water white appearance. Now titrate back with a standard solution of potassium permanganate until one or two drops of the latter render the test the faintest pink. Then add the sulphate standard again until this faint pink is changed to almost water white. Use 100 c.c. burettes and avoid a large excess of the sulphate.

**CALCULATIONS AND STANDARDS.**

*The permanganate standard* is made by dissolving 0.560 gram of KMnO<sub>4</sub> c.p. in water and diluting to 1 liter.

*The sulphate standard* is made by dissolving 13.7 grams of c.p. ferrous ammonium sulphate in water and diluting to 2 liters.

1 c.c. of this standard should equal from 0.000195 to 0.000198 gram of metallic manganese. Standardize either with a similar steel which has been carefully determined either by the method given on pages 188, 193, or 201, or add 0.050 gram of c.p.  $\text{KMnO}_4$  to a low manganese steel containing, for example, 0.23 per cent of manganese, and put it through all of the operations. Such a mixture will contain  $0.050 \times 0.3476$  or 0.01738 gram of Mn from the  $\text{KMnO}_4$  and 0.00023 gram of Mn from the 0.100 gram of steel, making a total of 0.0176 gram of Mn. The mixture should require from 89.8 to 90.6 c.c. of the sulphate standard if the directions are carried out exactly as given.

If the steel contains chromium it must be dissolved in 1 : 3 sulphuric acid and the chromium removed with zinc oxide. Dissolve 1 gram in 50 c.c. of 1 : 3  $\text{H}_2\text{SO}_4$  in a 500 c.c. volumetric flask, boil with 40 c.c. 1.20  $\text{HNO}_3$ , dilute to 300 c.c., add a slight excess of the zinc oxide, dilute to the mark, mix well, filter through a dry filter, fill a 100 c.c. burette with the filtrate and measure 50 c.c. into the 500 c.c. flask, add 350 c.c. of 1.20 nitric acid and finish as above. Put the above standardizing mixture through the same operations, including enough potassium dichromate to equal the chromium content of the test.

*The persulphate method:* Dissolve 0.100 gram of the sample in a liter boiling flask in 250 c.c. of 1 : 3 sulphuric acid and then add 100 c.c. of 1.20 nitric acid and boil gently 20 minutes. Remove from the heat and add 150 c.c. of silver nitrate solution (10 grams dissolved in a liter of water). Next add 200 c.c. of persulphate of ammonium (480 grams dissolved in 2 liters). Place again on the stove and heat at about 60° C. until all frothing is over and until practically no more fine bubbles continue to form in the solution. This will require about 45 minutes heating at the above temperature. Cool in running water and titrate the purple solution with the same standards as given in the similar lead peroxide method. Titrate cold. Separate chromium if present as in the lead peroxide method. The sulphate standard has the same value in metallic manganese as in the latter method.

Sample.	Phosphate.	Results by the different methods.	
		Lead peroxide.	Persulphate.
No. 40	Mn 14.84	14.76 14.92	14.85 14.77
39	9.04	9.00 9.10	9.03 9.11

NOTE. Titration with arsenious acid is objectionable in such high per cents of Mn as it gives brown tints that obscure the end point.

## CHAPTER XII.

### PART VI.

#### THE DETERMINATION OF MANGANESE IN 24 PER CENT NICKEL STEEL CONTAINING MANGANESE IN EXCESS OF TWO PER CENT.

THE ferricyanide method cannot be used on account of the interference of the nickel. Dissolve 1.0 and 0.9 gram for a check in 50 c.c. of 1.20 nitric acid. Rinse the solution into a liter volumetric flask; add 25 c.c. additional to insure a large excess of acid. Add a thick cream of manganese-free zinc oxide to the solution which has been diluted beforehand to 500 c.c. with water. Add the oxide rather slowly until the hydroxide of iron separates out, mixing the contents of the flask well with each addition of the oxide, by giving the flask a swirling motion. In order to be certain that the oxide is in excess, the separated precipitate should have a light brown to whitish brown appearance rather than a dark red. The contents of the flask are then diluted to the mark and all is then mixed by inverting the flask 5 times. Permit the precipitate to settle and then decant the supernatant fluid through a dry 15 c.c. filter into a dry beaker. By means of a 100 c.c. burette that has been rinsed three times with some of the filtered solution, measure off a 500 c.c. and a 250 c.c. portion of the filtered solution into 1000 c.c. boiling flasks, and titrate the aliquot parts in the manner described on page 49, using a permanganate standard of which 1 c.c. equals about 0.001 gram of manganese. When making these titrations with such a weak standard the operator may be uncertain as to the end point, as small particles of manganese hydrate that are held in suspension may give a pinkish effect to the supernatent fluid during the titration. It is therefore best to filter off a few drops of the pinkish appearing fluid through

washed asbestos that has been previously boiled with some rather concentrated permanganate solution and afterwards washed free of pink color. The asbestos so prepared will not bleach a few drops of even a very slightly pink test.

#### STANDARDIZATION.

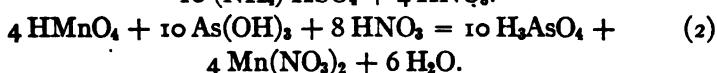
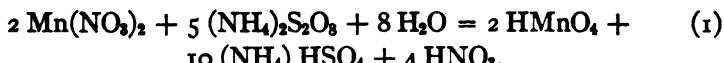
Dissolve and put through all of the above operations the following known mixtures: (1) 0.9 gram of iron containing no manganese, or a small known amount, 1.5 gram of the double sulphate of nickel and ammonium, and 0.140 gram of the purest permanganate of potassium; (2) 1.0 gram of manganese-free iron, 1.60 gram of the nickel salt and 0.150 gram of the permanganate. Mixture (1), assuming the full value of the permanganate to be present, should contain  $0.140 \times 0.34759$  or 0.04866 gram of manganese. As 500 c.c. were measured, or one-half, then 0.02433 gram of metallic manganese was titrated; this required 25.8 c.c. of the standard to produce a permanent pink; therefore 0.02433 divided by 25.8 equals 0.00094, or 1 c.c. of the standard equals 0.00094 gram of metallic manganese. By the same process (2) gave a value of 1 c.c. equals 0.00104 gram of manganese. The average of the two gives 1 c.c. equals 0.00099 gram of manganese.

## CHAPTER XII.

### PART VII.

#### DETERMINATION OF MANGANESE IN STEEL BY THE PERSULPHATE METHOD.

THE use of ammonium persulphate and silver nitrate for the determination of manganese in steel was first worked out in the United States by Walters. Ledebur in his *Leitfaden für Eisenhütten Laboratorien* refers to it as the method of Proctor Smith. The silver nitrate acts as an oxygen carrier by the intermediate formation of silver peroxide. The equations showing the action of the persulphate and the arsenious acid and the permanganic acid are given below:



Ledebur proceeds as follows: "0.2 gram of iron is dissolved in a beaker, in 15 c.c. of sulphuric acid (1 part of concentrated acid diluted with 2 parts of water) to which has been added 3 c.c. of 1.20 nitric acid. In the case of grey iron the graphite is filtered out and the filter is washed a number of times with water containing a drop or two of sulphuric acid. (The author suggests the dilute sulphuric wash as Ledebur does not specify the kind of a wash to use.) As a conveyor of oxygen, 10 c.c. of silver nitrate solution (5 grams of the silver salt dissolved in a liter of water) are added to the sulphuric acid solution of the iron and thereupon 15 c.c. of ammonium persulphate made by dissolving 60 grams of the persulphate in a liter of water."

"The solution of the sample is then heated as long as gas bubbles form in the same and until the last traces of persulphate are

decomposed. This can be usually accomplished by heating over a Bunsen burner for a minute. The careful adhering to these directions is important as it is easy to get too high results, if the persulphate is imperfectly decomposed, in that during the titration with arsenious acid a partial reoxidation of the reduced manganese salt or a slight reaction of the persulphate with the arsenious acid may occur."

"If during the oxidation of the manganese solution no red color forms then the solution is not sufficiently dilute. One can then add 20 c.c. of water, a further quantity of the persulphate and heat again. The heating should not exceed 60° C. at any time during the treatment with silver nitrate and persulphate."

The writer would suggest that the above directions which he has translated from Ledebur would have to be deviated from to suit the case as regards the amount of sample taken, for instance it would not be advisable to take 0.2 gram of a steel containing 2 or 3 per cent of manganese. In such high per cents from 0.1 to 0.05 gram would be quite enough to insure accuracy.

Ledebur titrates the cold solution, after diluting it with 50 c.c. of water, with a solution of arsenious anhydride made by dissolving 0.4 gram of the finely powdered oxide by warming it with 1.5 gram of anhydrous sodium carbonate dissolved in a little water. When the arsenious anhydride is dissolved it is diluted to one liter.

## CHAPTER XII.

### PART VIII.

#### SILICON IN PIG IRON, STEEL AND MUCK BAR.

WEIGH 1.5 grams of pig iron into a No. 2 dish. Add 15 c.c. 1 : 3 sulphuric acid \* plus 10 c.c. water. Weigh 5 grams of low silicon steel or 3 grams of high silicon steel, i.e., silicon content of 0.1 per cent and over, into a No. 5 dish. Add 45 c.c. 1 : 3 sulphuric acid and 25 c.c. of water. Warm gently until all metal is in solution, adding more water if necessary, should sulphate of iron form before effervescence is over. When the iron is in solution evaporate the pig iron and higher carbon steels directly to thick fumes of sulphuric anhydride without removing the covers.

Low carbon steels and chrome steels of 1 per cent chromium and over will bump and spurt from under the covers if attempt be made to evaporate them rapidly over the bare flame of the Argand burner. In such cases the covers are rinsed off into the dishes, and the contents of the latter are evaporated to thick fumes on a graphite or sand bath. (See page 415.)

For effecting the solution of the iron and the evaporation of fumes with covers on, an apparatus consisting of a stand of twelve Argand burners covered with a copper-rimmed asbestos board of twelve holes is used. (See Fig. 16, page 258.)

Having evaporated the samples to fumes, the dishes are cooled and filled conveniently full of distilled water. They are put on the heating stand; the contents heated and stirred until all of the sulphate of iron is in solution. Ashless paper pulp is mixed with the solutions, which are then filtered through 11

\* Use rubber stoppers in reagent bottles that are in constant use in routine silicon work, as during continued handling the glass stoppers are struck against the necks of the bottles and small chips of glass are knocked off into the acids causing high results.

cm. ashless filters; the silicious residues washed free from iron test with 1 : 10 hydrochloric acid and then free of acid with water. Potassium sulphocyanate is used in testing for the presence of iron. Wash acid and wash water are applied cold.

The washed residues are ignited in a muffle furnace until pure white.\* The residues may retain a reddish tint due to iron, or may be colored grey from presence of chromium or copper oxides, or yellow owing to the presence of small quantities of tungsten or vanadium. In such event after having been weighed they should be evaporated to dryness with a few drops of sulphuric acid and 10 c.c. of c.p. hydrofluoric acid. They are then ignited and weighed again, and the silicon content is calculated from the loss of weight, which multiplied by 47.02 and divided by the weight taken, yields the percentage of silicon.

When chromium is present, to the extent of 1 per cent, the silica residue can be freed sufficiently from chromium to make a subsequent evaporation with hydrofluoric and sulphuric acids unnecessary by boiling the fumed sulphate residue for ten minutes with a mixture of 75 c.c. of 1 : 1 hydrochloric acid and 75 c.c. of water. Then filter and wash as before.†

The ignited residues are cooled in a desiccator, weighed, multiplied by 47.02 and divided by the weight taken.

The silicious residues obtained by this method, or any other of the variations that are in vogue, are liable to be contaminated with titanium and aluminum, especially, in pig iron. Hence all silica residues, for strictest accuracy, should be evaporated with an excess of hydrofluoric acid and two or three drops of sulphuric acid, then ignited and weighed again, multiplying the loss of weight by the usual factor, and dividing by the weight taken to obtain the percentage of silicon.

\* The writer uses an electrically heated muffle ventilated by a slow stream of compressed air.

† For close work it is always advisable to use the hydrofluoric acid when chromium is present.

## CHAPTER XII.

### PART IX.

#### THE ANALYSIS OF CALCIUM ELECTRO-SILICON.

0.9 or 1.0 gram of the floured sample is fused with 20 grams of anhydrous sodium carbonate ground with 2 grams of niter in a platinum crucible. The analysis is proceeded with as in crucible slag (page 110), obtaining residues *A* and *B* which contain all of the silicic acid and perhaps a small portion of the calcium, iron, etc. This residue is weighed and hydrofluoric acid is added to it very slowly at first and finally enough of this acid to fill the crucible two-thirds full. Before the HFl, ten drops of conc. sulphuric acid are added. Then evaporation to fumes follows and the silicon is finished as in steels. Where such large amounts of silica are evaporated it is well to add more HFl and sulphuric acid and repeat the volatilization to make sure that all of the silica has been removed. The stain or residue remaining in the crucible after these evaportations is fused with a gram of sodium carbonate, dissolved out with HCl and added to the combined filtrates from *A* and *B* which will now contain all of the iron, aluminum manganese, calcium and magnesium. A double basic acetate separation of the iron as given on pages 188 and 189 is made. The acetate precipitate from the second precipitation is ignited, dissolved in HCl, precipitated with ammonia, washed, ignited, and weighed as oxides of iron and aluminum. These oxides are then dissolved in HCl and the solution is divided into two equal parts. One-half is reduced with stannous chloride and finished for iron as in iron ore. The other half is converted into nitrate and finished for phosphorus as in steel. The iron is multiplied by two, calculated to ferric oxide and deducted from the total oxides. The phosphorus is also multiplied by two, calculated to P<sub>2</sub>O<sub>5</sub> and deducted

from the total oxides. The remainder after these deductions is calculated to metallic aluminum.

The filtrates from the two basic acetate precipitations contain all of the calcium which is precipitated with ammonium oxalate and finished in the usual way as in limestone. The manganese is obtained as in tungsten, page 71.

ANALYSIS.

	Per cent.		Per cent.
Silicon.....	58.48	Calcium.....	30.86
Iron.....	7.08	Carbon.....	0.80
Aluminum .....	2.41	Manganese.....	0.06

The carbon is gotten by ignition of 0.5 gram of the sample with 4 grams of red lead, or litharge, in the electric furnace.

## CHAPTER XIII.

### PART I.

#### THE DETERMINATION OF URANIUM IN FERRO-URANIUM, CARNOTITE ORE AND MIXTURES OF IRON, VANADIUM, URANIUM AND ALUMINUM.

THE determination of uranium in ores and ferro-alloys is usually complicated by the presence of vanadium and aluminum. The writer has encountered so-called ferro-uranium containing as much as from 15 to 20 per cent of aluminum in several instances. Vanadium was always present from 2 or 3 per cent to as high as 28 per cent.

The scheme of titrating the uranium and vanadium together by reducing both elements in sulphuric acid solution with aluminum was tried as recommended by some writers. In this method the total amount of the permanganate standard required to reoxidize both elements so as to produce a slight permanent pink color is noted. Then the vanadium, alone, is reduced, this time to  $V_2O_4$  only, by adding an excess of sulphurous acid ( $SO_2$ ) and boiling off the excess of the latter. The vanadium is then oxidized back until a slight permanent pink is again obtained. The number of c.c. of the  $KMnO_4$  required in this second titration is multiplied by three and deducted from the amount of the permanganate used in the first titration. The remainder is multiplied by the uranium value of the permanganate, thus obtaining the uranium. In the writer's hands the results were discordant whether the reduction was accomplished by aluminum or zinc. The more vanadium present the worse disagreements, and the less vanadium, the more nearly the true uranium was obtained. With uranium, alone, the reduction with permanganate is entirely satisfactory.

During these experiments the writer tried hydrogen sulphide

as a reducing medium and found that H<sub>2</sub>S reduces both vanadium and iron but *does not reduce the uranium*. This afforded a way of determining the vanadium in the presence of the uranium but has no advantage over the method of the writer, to be described. The H<sub>2</sub>S reduction makes it possible to determine both iron and vanadium in the presence of uranium, in fact to determine all three elements. The uranium and iron together with the vanadium carried by them can be precipitated by a slight excess of ammonia; washed with ammonium nitrate water; ignited at a low red heat; moistened with conc. nitric acid; ignited again at a low red; cooled and weighed as Fe<sub>2</sub>O<sub>3</sub>, U<sub>3</sub>O<sub>8</sub> and some V<sub>2</sub>O<sub>5</sub> (all of the V<sub>2</sub>O<sub>5</sub>, if sufficient of the Fe and U be present). The weighed oxides are dissolved in HCl; evaporated with 40 c.c. of 1 : 3 H<sub>2</sub>SO<sub>4</sub> to thick fumes; dissolved in 150 c.c. of water and the vanadium and iron in the mixture determined as given on page 29, reducing with H<sub>2</sub>S. The Fe and V so found are calculated to the proper oxides and deducted from the weight of the total oxides above mentioned and the uranium oxide is thus obtained by difference. Similarly, U and Fe alone can be analyzed, getting the iron by the H<sub>2</sub>S reduction and the uranium by difference. Also should aluminum be present, the total oxides, after being weighed, can be dissolved, the solution be divided into two equal parts and one part analyzed as above for the Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>, and the other part analyzed for aluminum oxide as given in the method about to be described. Deduct twice the Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> + V<sub>2</sub>O<sub>5</sub> found from the weight of the total Al<sub>2</sub>O<sub>3</sub> + U<sub>3</sub>O<sub>8</sub> + V<sub>2</sub>O<sub>5</sub> + Fe<sub>2</sub>O<sub>3</sub>, obtaining the U<sub>3</sub>O<sub>8</sub> by difference.

The author devised, tested, and is now using the following method for the determination of uranium in carnotite, ferro-uranium and steel: For carnotite ores containing, as they usually do, from 1 to 4 per cent of U<sub>3</sub>O<sub>8</sub> weigh 2 grams and 3 grams for a check. For ferro-uranium do not take over 1 gram, and a half gram for a check. Dissolve or extract the samples, first with 100 c.c. of conc. nitric acid for an hour. Evaporate to dryness in the casserole, using a Royal Berlin,

porcelain handled casserole, of  $4\frac{1}{2}$  inches diameter. Take up in 100 c.c. of conc. HCl, evaporate to 20 c.c., dilute with 50 c.c. of water and filter out the insoluble residue consisting mainly of silica. Wash with dilute HCl about fifty times. Dilute to 300 c.c.; nearly neutralize with ammonia; and pass H<sub>2</sub>S in hot solution to remove any Mo, Pb, Sn, Cu, As, Bi or Sb that may be present. Filter; wash with H<sub>2</sub>S water, thoroughly, and evaporate the filtrate and washings to 20 c.c.; add an excess of chlorate of potassium, about 1 gram to destroy the H<sub>2</sub>S, also 50 c.c. of HCl, conc., and heat, covered, until all spraying is over and evaporate to 20 c.c. Transfer to a liter boiling flask; add sodium peroxide from a porcelain spoon to the 300 c.c. solution in the flask until a slight excess is obtained. (It should be said that the above mentioned insoluble residue is evaporated with an excess of HFl and 10 drops of conc. H<sub>2</sub>SO<sub>4</sub> and the remaining residue is fused with sodium carbonate; the fusion is dissolved out with HCl and added to the main solution in the liter flask before commencing the addition of the sodium peroxide.) When an excess of peroxide has been added to the solution in the liter flask, then 10 grams of ammonium carbonate are added to the alkaline solution; next in order, 10 grams of sodium carbonate are put in, and last of all, 10 grams excess of sodium peroxide are added. The solution is now just brought to incipient boiling, and immediately removed from the flame; cooled; paper pulp is added and the solution is filtered from the iron on the filter is washed with a mixture consisting of 5 grams each of sodium and ammonium carbonates, dissolved in 500 c.c. of water. The filtrate and washings, which should have a volume of not less than 400 c.c., are now neutralized with 1 : 1 HCl, added until the solution no longer immediately turns a narrow strip of turmeric paper, to the faintest brown. If there be alumina present to the extent of even a half per cent, it will have clouded the solution long before the turmeric ceases to be affected by the solution. Let the latter stand for at least an hour and then the aluminum can be filtered out, and washed

with ammonium nitrate as given previously (5 grams of the salt to 500 c.c. of water).

If the titration with acid is carefully done the filtrate and washings will not contain aluminum even though there be in the solution the equivalent of 0.100 gram of Al. The filtrate and washings from the aluminum will contain all of the U and much of the V, if the iron present does not exceed more than the equivalent of 0.100 gram of iron. The iron can be dissolved off the filter, peroxidized a second time as before and the alkaline filtrate and washings obtained, keeping them separate from the filtrate and washings obtained from the first peroxidation. These two filtrates and washings are then made entirely acid after the removal of the aluminum, and boiled for one hour, or until all CO<sub>2</sub> is removed from the solution, which will be accomplished when there are no longer any more lines, or fine threads of bubbles coming up through the solution. Then the uranium together with considerable vanadium is precipitated out with a *slight* excess of ammonia. The solution is boiled gently for a half hour. If much vanadium is present, the precipitate will be more of a green than a yellow; but if much uranium and little vanadium be present, then the precipitate will take on a bright yellow color, especially after heating for a time. The precipitate which consists mainly of uranium vanadate is filtered off and washed with the ammonium nitrate wash (5 grams to 500 c.c. of water). After a few washings, the precipitate is dissolved off the filter to get rid of any occluded salts, reprecipitated, and washed as before. The precipitate is now ignited in a platinum crucible, or a porcelain one if the platinum one is not available, and ignited at a low red heat, after the paper has been smoked off. The ash is moistened with a few drops of conc. nitric acid, and again heated to a low red heat; cooled; and weighed as U<sub>3</sub>O<sub>8</sub> plus V<sub>2</sub>O<sub>5</sub>. The weighed oxides are dissolved \* in conc. H<sub>2</sub>SO<sub>4</sub>; transferred to small casseroles and evaporated low with 50 c.c. of

\* Do not use HCl at this point as chlorine would be generated and the platinum badly attacked. Use 10 c.c. conc. H<sub>2</sub>SO<sub>4</sub> and heat for an hour, or until dissolved.

HCl. This solution is then evaporated to thick fumes, with 40 c.c. of 1 : 3 H<sub>2</sub>SO<sub>4</sub>; cooled; diluted with water; filtered from the small amount of silica usually present which is washed with dilute sulphuric acid; ignited and weighed; and deducted from the U<sub>3</sub>O<sub>8</sub> plus V<sub>2</sub>O<sub>5</sub>. The filtrate and washings from this silica contain the vanadium that was precipitated with the uranium. Owing to the evaporation with the large excess of HCl, the vanadium is now reduced to V<sub>2</sub>O<sub>4</sub>. It can be titrated to a permanent pink with the standard permanganate solution, and the vanadium so found is calculated to V<sub>2</sub>O<sub>5</sub> and subtracted from the silica free weight of the above oxides, thus giving the uranium by difference. Also the filtrate and washings from the small amount of silica can be heated to boiling and permanganate solution added cautiously so as to maintain a pink solution but not in such excess as to produce a heavy precipitate of manganese oxide as that would make a filtration necessary.\* The boiling is continued for twenty minutes. If the solution still remains pink with perhaps a very slight precipitate of the manganese oxide, then it is certain that all organic matter that may have crept in during the analysis is rendered harmless as far as affecting the permanganate standard during the subsequent titration is concerned. The ferrous ammonium sulphate standard is now added to the hot solution until the pink color is just removed and any slight "cloud" of precipitated manganese oxide is also dissolved, leaving the solution perfectly clear. The solutions of the tests are now cooled, and an excess of the permanganate standard is added to all of them. Then one of them is titrated drop by drop with the sulphate standard until three drops at room temperature give but a faint pink that remains practically unchanged for one minute. This is the start-

\* Of course there is no objection to boiling with an excess of the manganese oxide except the extra operation involved. Indeed the author has had cases where, owing to carbonaceous matter having gotten into the work, probably by extraction from filter papers, or mechanically, it was deemed advisable to boil with an excess of permanganate sufficient to produce a precipitate that remained even after a half hour of boiling. This brown oxide is filtered out through a porous thimble and the vanadium titrated exactly as described on page 35.

ing point of the titration with the ferrous ammonium sulphate standard. The volume should now be not over 200 c.c. Add  $\frac{1}{2}$  c.c. of the ferricyanide indicator (5 grams of the salt dissolved in 130 c.c. of water) and then the ferrous ammonium sulphate standard with vigorous stirring until three drops change the dark green color that forms to a distinct blue, i.e., to the first real blue. The number of c.c. of the sulphate standard required to produce this blue, after the addition of the indicator, multiplied by the vanadium value of the sulphate gives the vanadium that was carried out with the uranium. It is calculated to  $V_2O_5$  and the uranium is thus obtained by difference. The  $U_3O_8$  so found can be calculated to metallic U by the factor 0.8482. To standardize the permanganate and sulphate standards for vanadium, it is convenient to weigh 0.08 and 0.04 gram of vanadium pentoxide of known purity into small casseroles; dissolve in 60 c.c. of conc. HCl; evaporate low; fume with 40 c.c. of 1 : 3  $H_2SO_4$  and carry through all of the operations leading up to the titration with  $KMnO_4$  and the final titration with the sulphate. This will give the blank to deduct from each method of titration of the vanadium.

For checking methods and manipulations the writer used c.p. uranium nitrate and uranium acetate  $UO_2(NO_3)_2 + 6H_2O$  and  $UO_2(C_2H_3O_2)_2 + 2H_2O$ , respectively.

A mixture that approximates to the general run of carnotite ores of the Colorado mines is 0.100 gram of uranium nitrate, 0.100 gram of the Sibley iron ore standard; 0.050 gram of aluminum, and 0.040 gram of  $V_2O_5$ . (The latter can be obtained of 99.5 per cent  $V_2O_5$ .) As a further check, the author often runs a mixture of double the above amounts of uranium salt, the oxide of vanadium, and iron ore. These mixtures are put through all of the operations described.

#### CALCULATIONS.

For the benefit of those who wish to try the reduction with aluminum to check the purity of uranium nitrate, or who may wish to assay uranium obtained from a source that is free of

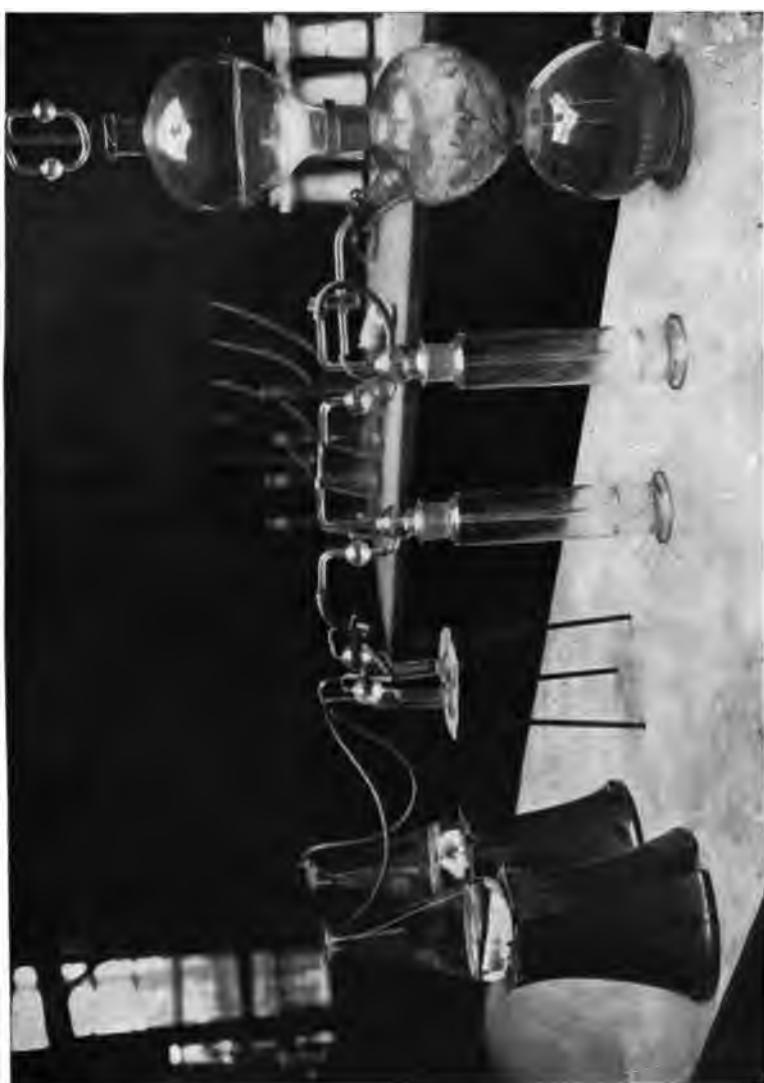


Photo No. 21.

vanadium, the method in general is to convert to sulphates, and heat in cone flasks in the presence of an excess of from 20 to 30 c.c. of conc.  $H_2SO_4$  diluted to 100 c.c. with water. A coil of 18 gauge aluminum wire of  $\frac{1}{16}$  inch diameter and about 7 inches long \* is placed in the solution, and the latter is heated to nearly boiling for 2 hours with a stream of purified  $CO_2$  passing through a perforated watch glass into the cone flask to prevent the entrance of air. The  $CO_2$  is generated by the action of  $HCl$  (1 : 1) on marble and passes through a wash bottle containing an inch of water and then through another bottle containing a similar depth of a saturated solution of sodium carbonate. After the two hours reduction, the solution is cooled with  $CO_2$  passing, and when cold the aluminum coil is removed and the solution is titrated with N/40  $KMnO_4$  to a slight permanent pink. A blank is also run at the same time and deducted. A solution of N/40 should equal 0.00298 gram U per c.c. The equation is  $2 KMnO_4 + 5 UO_2(SO_4)_2 + 2 H_2O = 2 KHSO_4 + 2 MnSO_4 + 5 UO_3(SO_4) + H_2SO_4$ .

The permanganate is standardized with sodium oxalate (see page 42).

By the above equation we see that 2 gram molecules of  $KMnO_4$  equal 5 gram atoms of U. On page 388 it was explained that  $\frac{1}{5}$  of the gram molecule of permanganate constitutes its normal solution when dissolved in a liter volume. Hence,  $2KMnO_4 = 5U$ , or  $KMnO_4 = \frac{5U}{2}$ , so that  $\frac{1}{5}$  of the gram molecular weight or normal  $KMnO_4$  would equal  $\frac{1}{2}$  the gram molecular weight of uranium or 119.25 gram of U. Therefore 1 c.c. of the N/40  $KMnO_4$  is equal to  $\frac{119.25}{40,000}$ , or 0.00298 gram of U. Having found by titration the value of the permanganate standard per c.c. in sodium oxalate as given on page 42, the following give the values of the N/40 permanganate in U, V and Fe.

\* See photo No. 21.

The value of N/40 KMnO<sub>4</sub> per c.c. in gram of sodium oxalate

multiplied by  $\frac{238.5}{134}$  equals its value in gram of U per c.c.

by  $\frac{102.0}{134}$  equals its value in gram of V per c.c.

by  $\frac{111.7}{134}$  equals its value in gram of Fe per c.c.

The percentage of uranium in uranium nitrate is 47.45.

The percentage of uranium in uranium acetate is 56.17.

The percentage of uranium in uranoso-uranic oxide (U<sub>3</sub>O<sub>8</sub>) is 84.825.

The percentage of vanadium in vanadium pentoxide is 56.04.

From a standardization as above, the author, for example, found that 1 c.c. of N/40 KMnO<sub>4</sub> equals 0.00167 gram of sodium oxalate.

1 c.c. of N/40 KMnO<sub>4</sub> equals 0.00297 gram of uranium.

1 c.c. of N/40 KMnO<sub>4</sub> equals 0.001276 gram of vanadium.

The following are the calculations for an actual analysis of a mixture: 0.100 gram of uranium nitrate crystals, 0.100 gram of the Sibley iron ore standard, 0.05 gram of metallic aluminum, and 0.040 gram of V<sub>2</sub>O<sub>5</sub> of 99.5 per cent purity were put through all of the operations in the method as described and the following analytical data were obtained:

(1) 58.8 c.c. of sulphate were required to remove all pink and brown tints from 60 c.c. of the KMnO<sub>4</sub> standard (N/40) placed in a beaker with 40 c.c. of 1 : 3 sulphuric acid and 200 c.c. of distilled water. As 1 c.c. of the N/40 KMnO<sub>4</sub> was found equal to 0.001276 gram of V then 1 c.c. of the ferrous ammonium sulphate standard is equal to 0.001276 × 60 divided by 58.8 or 0.0013 gram of V.

(2) The U<sub>3</sub>O<sub>8</sub> + V<sub>2</sub>O<sub>5</sub> obtained, in the course of the analysis, from the above mixture weighed 0.076 gram after deducting 0.0014 gram of silica found in it on dissolving in HCl.

(3) Beginning at the point where the U<sub>3</sub>O<sub>8</sub> plus V<sub>2</sub>O<sub>5</sub> were dissolved in HCl; evaporated with 40 c.c. of 1:3 H<sub>2</sub>SO<sub>4</sub> to thick

fumes, etc., 0.020 and 0.040 gram of the  $V_2O_5$ , alone, were put through all of the subsequent operations and the vanadium therein was titrated with the sulphate standard as already described. The 0.020 gram required 10.1 c.c. of the sulphate to produce the blue end point, and the 0.040 consumed 18.8 c.c. (Blank and all). The 0.020 gram of  $V_2O_5$  contains  $0.020 \times 0.995 \times 0.5604$  equals 0.01116 gram V. Now we saw by (1) that the sulphate standard has a value of 1 c.c. equals 0.0013 gram of V, hence the sulphate required to unite with the vanadium present will equal 0.001115 divided by 0.0013 or 8.6 c.c. This gives 10.1 c.c. minus 8.6 c.c. or a blank of 1.5 c.c. to be deducted from all tests.

(4) The  $V_2O_5$  in (2) was determined in like manner and found to require 9.5 c.c. of the sulphate. We have just seen that the calculated blank is 1.5 c.c., therefore the actual V in (2) required 9.5 minus 1.5, or 8 c.c. Then the  $V_2O_5$  in (2) is equal to  $0.0013 \times 8$  divided by 0.5604 or 0.0185 gram. Hence the  $U_3O_8$  in (2) equals 0.076 minus 0.0185 or 0.0575 which is equivalent to 0.0487 gram of uranium. The uranium contained in the uranium nitrate taken equals  $0.100 \times 0.4745$  or 0.04745 gram of uranium. This gives an excess of 0.0012 gram of U found, which was in all probability due to the presence of a little Al that was not removed by the neutralization with the 1 : 1 HCl. The author would recommend that the operator exercise great care in the neutralization. The acid should be added until, as already stated, a narrow strip of turmeric paper dipped into solution does not show any more change than a similar strip dipped in water. It is also advisable, for close work, to allow the neutralized solution to stand for twelve hours before filtering out the aluminum hydroxide.

It must be remembered that when a very large quantity of iron, for instance 0.400 gram of iron, is to be separated from much uranium, say about 0.200 gram of U and 0.100 gram of Al, then at least three peroxidations will be required, made as described under carnotite, to remove all of the U and Al away from the iron. Then when the Al is separated from the U by the acid precipi-

tation, the Al is almost certain to carry out with it 2 or 3 mgs. of  $\text{U}_3\text{O}_8$ . This latter can be removed by redissolving the Al in the hot 1 : 1 HCl; the solution of the Al is treated with an excess of sodium peroxide, i.e., the peroxide is added to it in a liter boiling flask to strong alkaline reaction; then add 5 grams each of sodium carbonate, and ammonium carbonate, and 5 grams sodium peroxide. Bring just to the boil; cool and precipitate, as already described, to the turmeric neutral point with 1 : 1 HCl; let stand for 12 hours and filter out the Al which will now be free of U. The filtrate from the Al is made acid; boiled until free of  $\text{CO}_2$ ; and the small amount of U is precipitated with ammonia in slight excess, boiling gently for 30 minutes. The U is filtered out; and added to the main portion of the U before it is precipitated with ammonia the first time.

Most ferro-uranium and ferro-uranium-vanadium-aluminum alloys will dissolve in a mixture of HCl and  $\text{HNO}_3$  but the author analyzed one such alloy that contained 15 per cent of silicon that could be decomposed only by fusing it twice with sodium peroxide. The following results attest the accuracy of the method:

Uranium added.	Uranium found.	Uranium added.	Uranium found.
gram	gram	gram	gram
0.047	0.048	0.071	0.0729
0.047	0.047	0.047	0.0468
0.094	0.0948	0.094	0.0950

#### URANIUM IN STEEL IN THE PRESENCE OR ABSENCE OF TUNGSTEN, CHROMIUM, ALUMINUM, COBALT, NICKEL AND VANADIUM.

*Qualitative.* Dissolve 1 gram of the steel by heating it with 40 c.c. of 1 : 3 sulphuric acid. When action is over add 15 c.c. of 1.20 nitric acid and heat further until red fumes are gone and the tungstic acid, if present, becomes bright yellow; dilute with 100 c.c. of water; warm for a half hour; filter out the tungsten and wash it with a dilute sulphuric acid water.

Dilute the filtrate and washings from the tungsten to 200 c.c. with water in a 1000 c.c. boiling flask and peroxidize exactly as described in the gravimetric method for carnotite. Filter out the iron, nickel, cobalt and copper and wash the filter a few times with the carbonate water. The filtrate and washings are then rendered just neutral to turmeric paper with 1 : 3 sulphuric acid. Allow the neutral solution to stand for several hours before filtering out any silicic acid or aluminum hydroxide that may form at this point. Filter, wash with ammonium nitrate wash; make the filtrate and washings acid with  $H_2SO_4$ ; boil the filtrate and washings gently until no more finely divided bubbles of  $CO_2$  form. Then make the solution slightly ammoniacal and heat for 15 minutes. Then remove from the flame when, if even 0.25 to 0.50 per cent uranium be present, it will give a considerable yellow precipitate of uranium hydroxide which will contain vanadium if the latter be present. If much chromium is present collect this precipitate on a filter to note its color, which should be yellow. Any aluminum hydroxide or silicic acid coming from the reagents and appearing at this stage when filtered off and washed with ammonium nitrate will not show yellow but will be white on the filter. The operator should add enough uranium nitrate crystals to 1 gram of a chromium-tungsten steel to equal 0.50 per cent of U and put it through all of the operations along with the steel that is to be tested and also 1 gram of the known steel without any uranium added and he can then compare the results obtained and be able to form a very sure conclusion as to the presence or absence of U in the unknown steel.

*Quantitative.* The gravimetric method is carried out exactly as the qualitative method except that the separations with the two carbonates and the peroxide are continued until there is no further formation of a yellow precipitate on redissolving the iron precipitate and making a further separation of the uranium as before. Then finish the determination as given for carnotite on page 294, beginning at the point where the uranium vanadate is filtered off and washed with the ammonium nitrate solution.

## CHAPTER XIII.

### PART II.

#### THE DETERMINATION OF VANADIUM IN SANDSTONES CONTAINING CARNOTITE, ROSCOELITE, AND CALCIUM VANADATE, ETC.

(A) If the sandstone contains about 3 per cent V then take 3 grams of the finely powdered ore, and 4 grams for a check analysis. Treat the ore in a Royal Berlin, porcelain-handled casserole, and extract it with 100 c.c. of conc. HNO<sub>3</sub> for a half hour, just below boiling, with frequent stirring. Then remove the cover and evaporate to dryness. In the same manner extract this residue with 50 c.c. of conc. HCl, heating with the cover on until all red fumes are gone. Now remove the cover, and evaporate low. Add 50 c.c. of 1 : 1 sulphuric acid and evaporate to heavy white fumes to remove the HCl. Cool. Add 50 c.c. of water, stir, heat, cool, filter off the insoluble residue and wash it with dilute sulphuric acid water. Dilute the filtrate and washings to 200 c.c., boil with permanganate and finish the determination as given on page 35.

(B) If the chemist wishes to reassure himself that even the last traces of vanadium have been extracted from the ore, he can burn off the insoluble residue obtained above in an iron crucible and fuse with 10 grams of peroxide of sodium. The fusion is kept hot enough to keep the peroxide just molten for two minutes. The fusion is then dissolved out in the manner described on page 140 under Chromium in Chrome Ore. The sulphuric acid solution is filtered from any iron scales and the filtrate and washings are then analyzed for vanadium as above, and any vanadium found is added to that gotten in the main solution.

It is well for the operator to put a known amount of vanadium through all of the operations described in (A) to get the vana-

dium value of the standards for this method. Ferro-vanadium of known vanadium content is decidedly the best for the manipulation under (A). For (B) vanadic acid ( $V_2O_5$ ) of known purity is much the best source of V.

Almost any ore of vanadium can be accurately assayed for vanadium by the combination of (A) and (B). The sulphide ore of vanadium (Patronite) should first have the sulphur roasted out of it at a low heat, when it can be analyzed according to (A) and (B) or the ash can be fused according to (B) alone.

## CHAPTER XIV.

### PART I.

#### QUALITATIVE AND QUANTITATIVE TESTS FOR COBALT AND NICKEL IN STEEL.

DISSOLVE 0.500 gram of drillings in a mixture of 30 c.c. 1.20 HCl and 30 c.c. of conc. nitric acid. Heat until the insoluble residue is bright yellow if tungsten is present. Filter on a double 11 cm. filter; wash free of iron with 1 : 10 HCl. Make one basic acetate separation as in the gravimetric method; filter, wash a few times with acetate wash. Evaporate the filtrate washings, if necessary, to 200 c.c. Now warm the solution with a drop or two of ammonia to see if any small amount of iron separates out. Filter again, as iron interferes with cobalt test, and wash a few times with ammonia wash; add an excess of dimethylglyoxime to the ammoniacal filtrate. If only a brown coloration results that does not turn to a scarlet precipitate, then cobalt is present. If a scarlet precipitate forms at once or in a few minutes then nickel is present (see Brunck's method for nickel).

If on filtering off this scarlet precipitate, after one hour's wait the filtrate is brown in color, then cobalt is also present. 0.25 per cent of cobalt in 0.500 gram of steel gives a very distinct brown color. The writer would suggest this for a color method for small amounts of cobalt. If only a slight brown coloration forms on adding the "dimethyl" then several hours should elapse before making a decision, as a small amount of nickel, at first, gives only a brown coloration which eventually changes to a small scarlet precipitate.

If a per cent or two of cobalt is present then the acetate filtrates will show a pink coloration which is in itself a sure proof of the presence of cobalt; i.e., before any "dimethyl" is added. This pink color looks exactly like a weak solution of KMnO<sub>4</sub>.

**QUALITATIVE TEST FOR COBALT IN STEEL IN THE PRESENCE OF NICKEL, IRON, CHROME, ETC.**

Dissolve 1 gram in nitric acid or in the before mentioned mixture of nitric and hydrochloric acid; boil down to 20 c.c.; add an excess of ammonia. Redissolve in glacial acetic acid; add a large excess of potassium nitrite and in a little time a yellow precipitate of potassium cobaltic-cyanide will separate out, and look very much like the yellow precipitate obtained with molybdate solution, in phosphorus analysis.

To prevent frothing add some alcohol immediately after putting in the potassium nitrite.

**GRAVIMETRIC METHOD FOR COBALT.**

*In steels either in presence or absence of tungsten, molybdenum, vanadium and chromium.*

Weigh 1 gram and 500 mgs. of sample and transfer to No. 5 Royal Berlin porcelain dishes. Dissolve each in a mixture of 30 c.c. conc. HCl and 30 c.c. conc. HNO<sub>3</sub>. When frothing is over, place over moderate flames on graphite baths and heat for about one hour, or until residue in dish is of a clean bright yellow color. Rinse off cover glasses and sides of dishes with water, then add 100 c.c. conc. HNO<sub>3</sub> and take to dryness, lowering flames to avoid loss from spouting when contents of dishes are nearly dry. (This is conveniently accomplished over night.)

Bake over a bare flame until nitric fumes are driven off. When sufficiently cool to prevent cracking the dishes, add 40 c.c. conc. HCl, and with cover glass on, digest for 30 minutes, or until all soluble constituents are in solution; boil to volumes of about 25 c.c.; dilute with water to about 100 c.c.; and evaporate to about 75 c.c.

Rinse off cover glasses into dishes, add pulp, filter on double 11 cm. S. & S. filters into 600 c.c. beakers. Wash precipitate, until free of iron, with a 1 : 10 HCl wash. Set aside filtrate which contains the bulk of the cobalt.

## TREATMENT OF THE PRECIPITATE.

Burn off in clean platinum crucibles to yellow powder, using nickel wire to break up hard particles. Weigh when cool, add 2 or 3 drops  $H_2SO_4$  and 10 c.c. hydrofluoric acid and drive off the  $SiF_4$  in a moderately warm muffle. When dry remove any outside dirt from crucible with damp cheese-cloth, drive off  $SO_3$  fumes with aid of a Bunsen or Chaddock burner flame, heating finally to redness; cool, weigh. Loss in weight represents  $SiO_2$ , which, multiplied by 0.4702, gives silicon. Calculate to percentage.

To contents of each crucible add 8 grams  $Na_2CO_3$ . Fuse with lids on for 15 or 20 minutes. Let cool slightly and extract the melts with hot water in platinum dishes. When salts are in solution, which should not require more than 10 minutes heating, remove the crucibles and rinse them thoroughly with water into dishes so that they contain no carbonate. Filter on double No. 9 cm. S. & S. filters. Discard this filtrate. Wash precipitate with water until free of alkali to phenolphthaleine. Burn off in same crucibles in which fusions were made. Weigh when cool.

Difference in weight between the final silicon free weight and this one represents  $WO_3$ , which, when multiplied by 0.7931, gives tungsten. To the final residue in the crucible is added 10 c.c. conc. HCl and the crucible is heated gently until contents are dissolved.

Transfer dissolved content of each crucible to its respective beaker which contains the main cobalt filtrate. Total cobalt is now in 600 c.c. beakers.

Nearly neutralize with ammonia. Dilute to about 400 c.c. with water. Heat to 80° C. and pass  $H_2S$  through for 20 minutes or until precipitate separates out distinctly. Remove and let settle for at least  $\frac{1}{2}$  hour. Filter on double 11 cm. filters into 600 c.c. beakers, washing precipitate with  $H_2S$  wash (2 drops 1 : 1 HCl, 500 c.c. water, sat. with  $H_2S$ ).

Precipitate contains  $MoS_3$  and other metals that are precipitated in acid solution. Ignite the sulphides at a low red heat in porcelain; extract with ammonia and filter; wash with fil-

tered ammonia water and again weigh. Loss in weight is  $\text{MoO}_3$ , of which 66½ per cent is molybdenum.

*Filtrate from Sulphides.* Concentrate to about 50 c.c., add 50 c.c. conc. HCl, then 1 gram  $\text{KClO}_3$  and concentrate to 30 c.c., keeping covered until all fumes of chloric acid are gone to prevent loss by spraying. Dilute to 150 c.c., add 50 c.c. conc. HCl, and evaporate to 50 c.c. volume, to remove, entirely, the free chlorine. Finally, dilute to 300 c.c. with water, add ammonia until a faint cloud forms that will not stir out. Then add 20 c.c. and 10 c.c. of ammonium acetate to the 1 gram and 500 mg. weights respectively. (2 c.c. = 1 gram ammonium acetate.\*)

Put on Argand burner stove and allow them to boil for about 2 minutes. Remove from fire; allow acetates to settle; filter through double 15 cm. filters into 600 c.c. beakers that have been previously boiled out with dilute HCl. Wash precipitate 15 or 20 times with acetate wash. Set aside filtrates. Dissolve precipitate in 50 c.c. HCl (1 : 1) by heating and pouring back and forth several times, then washing filter free of iron with 1 : 10 HCl wash. Make a second basic acetate separation, using 15 c.c. and 8 c.c. of ammonium acetate respectively for the 1 gram and 500 mg. weights. Filter into 600 c.c. beakers and wash as before.

#### THE COMBINED ACETATE FILTRATES.

If these filtrates contain much cobalt they will be pink. Heat to boiling; make faintly ammoniacal; add 5 c.c. of 1 : 1 ammonia in excess and last of all 50 c.c. sat. solution of microcosmic salt. Stir vigorously, otherwise bumping may break beakers. A blue precipitate forms which continuous stirring changes to a crystalline grape colored precipitate that settles rapidly, leaving a water-white supernatant liquid. Filter on 11 cm. filters into clean liter beakers, washing precipitates with water containing 4 c.c. ammonium acetate, until free of chlorides, testing a few drops of the acidulated washings with silver nitrate solution.

\* Use an ammonium acetate solution that has been made neutral, or very faintly alkaline with ammonia.

Burn off precipitates in weighed platinum crucibles over low flame at first, then increase to bright red heat; break up lumps with a nichrome or platinum rod. Cool, and weigh as cobalt, nickel and manganese pyrophosphates and a little  $\text{SiO}_2$  (C). Determine manganese in a separate portion by sodium arsenite titration, calculate to  $\text{Mn}_2\text{P}_2\text{O}_7$  and deduct. Dissolve contents of crucibles with (1 : 1) HCl; filter; wash with 1 : 10 HCl, then with water; burn and weigh small amount of silica and deduct from (C). The remainder is  $\text{Co}_2\text{P}_2\text{O}_7$ , of which 40.39 per cent is Co.

The filtrates and washings from the phosphates of Co, Ni and Mn usually contain a little Co and most of the Ni, etc., which are removed by saturation with  $\text{H}_2\text{S}$  in hot solution as follows: Heat the latter to 70 or 80° C., pass  $\text{H}_2\text{S}$  through for about 30 minutes. Black CoS and NiS are precipitated. Filter on double 11 cm. filters and wash about 50 times or until free of salts with water containing 2 grams ammonium acetate and saturated with  $\text{H}_2\text{S}$ . Burn off and weigh as CoO, of which 78.66 per cent is Co. Add this cobalt to that found from phosphate precipitation to get total cobalt. Deduct the Ni found on a separate portion.

The gravimetric method for cobalt powders and ferro-cobalt is the same as in Co steels except that but 0.5 gram is taken for the Co determination.

#### VOLUMETRIC METHOD FOR COBALT IN STEEL. (PRE-LIMINARY REMARKS.)

Cobalt cannot be titrated quantitatively with KCN, exactly, as nickel owing to interfering reactions that take place. If the attempt is made to titrate cobalt *alone* with cyanide and silver a black precipitate forms that obscures the end point. This is due to the formation of silver cobaltic-oxide.

The writer, after several months of experimenting, found that by the use of tartaric acid and by always having not less than 1 gram of iron in solution per 0.1 gram of Co and by strict adherence to the following details, titrations, even up to 100 mgs.

of cobalt, can be made with the most satisfying accuracy: Dissolve 0.8 gram and 1.0 gram of the steel in 40 c.c. of 1 : 3 sulphuric acid; add 15 c.c. of 1.20 nitric acid and digest the steel, if tungsten be present, until the latter is bright yellow; cool; add 12 grams of tartaric acid; dilute to 100 c.c.; add 90 c.c. of 1 : 1 ammonia; drop in a piece of litmus paper and then drop in 1 : 3 sulphuric acid from a burette with great care, until the litmus paper just turns from a blue to a red; then add exactly 4 c.c. of 1 : 1 ammonia in excess and no more, before titration with KCN.

The writer uses Kahlbaum's c. p. cobalt powder for standardizations. Its purity can be checked by the phosphate method as given for steels. Nickel in cobalt steels and metals is determined by Brunck's method.

It is extremely important to have the excess of ammonia in all tests and standardizations mixtures as nearly alike as possible. Varying amounts of free ammonia cause discordant results, apparently to a much greater degree than in the similar titration for nickel.

#### VOLUMETRIC DETERMINATION OF COBALT IN STEELS CONTAINING COBALT WITH OR WITHOUT TUNGSTEN, CHROMIUM, VANADIUM AND MOLYBDENUM.

Nickel and copper interfere and must be removed before any attempt is made to titrate the Co, or determined on separate portions and deducted.

Weigh 1 gram and 800 mgs. of sample, 50 mgs. and 40 mgs. of c.p. cobalt along with 1 gram and 800 mgs. of cobalt, nickel and copper-free steel for standards, and 1 gram of the same non-cobalt steel, alone, for a blank test, into 600 c.c. beakers with cover glasses. Add 40 c.c.  $H_2SO_4$  (1 : 3) to each, and when most of action is over, place tests on Argand burner stove\* over low flames and heat until all soluble material is dissolved; about  $\frac{1}{2}$  hour is required. With beakers kept covered, introduce 15 c.c.  $HNO_3$  (1.20) through the lips of the beakers; continue heating until all red fumes are driven off (15 min-

\* See page 258.

utes required). Remove tests from stove, rinse cover glasses and sides of beakers with cold water, bringing volume of each to about 100 c.c. Add 12 grams of powdered tartaric acid to each and stir until dissolved. Add an excess of ammonia or about 90 c.c. of 1 : 1 ammonia; cool and proceed with the neutralization as described under "Preliminary Remarks." Place beakers in pans containing cold water so as to bring the tests down to room temperature.

#### SOLUTIONS

Cyanide . . . . .	9 grams KCN	2000 c.c. H <sub>2</sub> O	
	2 grams KOH	1 c.c. = about 0.00067 — 0.00069 gram of cobalt.	
Silver Nitrate . . . . .	1.50 gram AgNO <sub>3</sub>		
	250 c.c. H <sub>2</sub> O		
Potassium Iodide . . . . .	50 grams KI		
	250 c.c. H <sub>2</sub> O		

Add exactly 4 c.c. ammonia (1 : 1) to each neutral test solution before beginning to titrate. It is very important that the excess of ammonia be the same for standards and tests. (See preliminary remarks.)

Add 2 c.c. KI solution, then exactly 2 c.c. AgNO<sub>3</sub> solution, which produce quite a turbidity. Stir and add KCN solution rapidly at first and slowly toward the end until the cloud just disappears. Record time at that moment and let stand 6 minutes. Record readings of "Silver" and "Cyanide" burettes.

At the end of 6 minutes clear up the newly formed cloud, slowly, with cyanide and add the amount thus used to that already consumed. Titration is now finished. Disregard any subsequent clouds that are almost certain to form. Titration of 1 gram of a non-cobalt steel, to get the relation between cyanide and silver, is the next step and is as follows: After dropping in the 2 c.c. of KI (from small pipette or graduate) and 2 c.c. AgNO<sub>3</sub> from burette, clear up carefully and slowly with KCN solution and record readings. Since all steel contains at least a trace of copper or nickel, this titration is made in order to eliminate any interference from this cause. This having been done add 10 c.c. KCN solution, then carefully bring on a faint cloud

with  $\text{AgNO}_3$  solution, just clearing with a drop or two of KCN to be sure of no appreciable excess. This titration gives the relative comparison of cyanide and silver solutions, showing that 1.1 c.c. of KCN equal 1.0 c.c. of  $\text{AgNO}_3$ .

The calculations are the same as in the similar method for nickel, page 311. Deduct any nickel found on a separate portion by Brunck's method or the modified form of it. It is quite unlikely that appreciable amounts of nickel will be found in cobalt steels. The same can be said of copper, although the latter can be removed beforehand by  $\text{H}_2\text{S}$ .

#### STANDARDIZATIONS AND CALCULATIONS.

Determine the blank first. Add 2 c.c. KI solution then 2 c.c.  $\text{AgNO}_3$  solution. Add KCN solution drop by drop until white cloud of  $\text{AgI}$  disappears. Take burette readings for silver and cyanide solutions; then add a known amount of cyanide, about 10 c.c., and titrate to a faint cloud with silver nitrate. Calculate silver nitrate in terms of cyanide, e.g.,

$$\begin{aligned} 11.1 \text{ c.c. KCN} &= 10.1 \text{ c.c. } \text{AgNO}_3 \\ 1 \text{ c.c. } \text{AgNO}_3 &= 1.1 \text{ c.c. KCN.} \end{aligned}$$

Standard mixtures:

- (1) 30 mgs. Kahlbaum's cobalt and 800 mgs. high speed steel.
- (2) 50 mgs. Kahlbaum's cobalt and 1 gm. high speed steel.
- (3) 80 mgs. Kahlbaum's cobalt and 1 gm. high speed steel.
- (4) Blank, no cobalt added and 1 gm. high speed steel.

Put the above mixtures through all of the foregoing operations until the point of titration; then add 2 c.c. KI solution, also exactly 2 c.c.  $\text{AgNO}_3$ ; then with constant stirring drop in KCN solution until the cloud disappears. Record first and last readings of burettes. Note the time. Wait exactly six minutes, then read the KCN burette and clear up the second cloud cautiously. Take reading and add it to former KCN reading. Deduct  $(2.0 \times 1.1)$  c.c. from the total KCN reading; the remainder represents KCN consumed by the cobalt.

## EXAMPLE.

0.050 gm. metallic cobalt used, which contains 97.21 per cent Co.

KCN to clear first cloud.	KCN to clear second cloud.	$\text{AgNO}_3$
0.0	71.2	14.0
69.9	73.9	16.0
69.9	2.7	2.0
2.7		X 1.1
72.6		2.2
<u>- 2.2</u>		
70.4 = 0.05 gm. $\times$ 0.972 gm. Co = 0.0486 gm. Co., or 1 c.c. KCN		
= 0.0006904 gm. cobalt.		

Titrate sample in exactly the same way as the standard mixtures. Since 800 mg. weights have a general tendency to go lower than 1 gm. weights for reason stated in the introduction, use the higher factor on those weights, viz.:

30 mg. Std. + 800 mg. steel.
1 c.c. KCN = 0.000704 gm. cobalt.
.....
50 mg. Std. + 1 gm. steel.
1 c.c. KCN = 0.0006904 gm. cobalt.
.....

800 mg. sample required 49.4 c.c. KCN. Therefore the steel contained  $49.4 \times 0.000704$  mg. Co or 0.03477 mg. Co. Hence per cent cobalt in sample equals  $0.03477 \div 0.8 \times 100$ , or 4.35 per cent cobalt.

1 gm. sample required 63.0 c.c. KCN. Therefore the steel contained  $63.0 \times 0.0006904$  gm. Co, or 0.04349 gm. Co, or 4.35 per cent cobalt.

## NICKEL IN COBALT STEELS.

Weigh 1 gm. and 0.9 gm. of sample into 400 c.c. beakers. Dissolve in 25 c.c.  $\text{H}_2\text{SO}_4$  (1 : 3) over moderate flame. Oxidize with 10 c.c.  $\text{HNO}_3$  (1 : 20); cool; add 5 gms. citric acid per gram sample taken. Make slightly ammoniacal; dilute to 300 c.c.; add 20 c.c. of a 2 per cent alcoholic solution of dimethylglyoxime; let stand 2 hours; filter on double 11 cm. filters; wash about 25 times with dimethyl wash (10 c.c. of 2 per cent dimethyl to 500 c.c. water). Dissolve by passing 25 c.c. 1 : 20  $\text{HNO}_3$  (cold) back and forth on the filter. Wash about 40 times with nitric wash (10 c.c. 1 : 20  $\text{HNO}_3$  to 500 c.c. water). Make filtrate

ammoniacal and repeat dimethyl precipitation to remove cobalt which is carried out with nickel in considerable quantity. Filter and wash as above. The precipitate should be bulky and of a brick red appearance. If not, make a third precipitation to insure complete removal of cobalt.\*

Volume of dissolved precipitate should be about 100 c.c. Boil about 10 minutes. Add 15 c.c.  $H_2SO_4$  (1 : 3); cool; add 2 gms. citric acid; make slightly ammoniacal, volume about 200 c.c.; titrate at ordinary room temperature in usual manner for nickel titration in plain nickel steel by the KCN method; calculate per cent nickel in sample.

When nickel is present along with cobalt in steels, run nickel standards in the same manner as described for cobalt standards, i.e., clearing up of first cloud after waiting 6 minutes. Per cent nickel having been determined by separate operation, calculate number of c.c. used for nickel by dividing amount of nickel found by the nickel value of the cyanide solution standardized as above; deduct from total KCN used by the cobalt plus nickel and calculate cobalt by multiplying the remaining c.c. by the cobalt value of the solution.

#### STANDARDIZATION OF KCN SOLUTION, WITH NICKEL AMMONIUM SULPHATE, FOR COBALT NICKEL STEELS.

200 mgs. Ni. Am. Sulphate.	800 mgs. High Speed Steel.	
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KCN to clear first cloud.	KCN to clear second cloud.	$AgNO_3$
19.3	58.0	48.0
51.6	58.4	50.0
32.3	0.4	2.0
— .4		
32.7		X1.1
2.2		2.2
30.5		

0.0146 gm. of Ni in 0.100 gram of Ni. Am. sulphate  
 $0.0146 \text{ gm.} \times 2 \div 30.5 = 0.000957$  or  
 1 c.c. KCN solution equals 0.000957 gm. nickel.

\* A filtrate at this point, free from brown color, indicates the complete removal of the cobalt from the red nickel precipitate.

QUANTITATIVE TESTS FOR COBALT AND NICKEL IN STEEL 313

340 mgs. Ni. Am. Sulphate.	1 gm. High Speed Steel.	
KCN	KCN	AgNO <sub>3</sub>
1.2	78.6	52.0
54.0	80.6	54.0
<u>52.8</u>	<u>2.0</u>	<u>2.0</u>
+2.0		
54.8		
2.2		
<u>52.6</u>		

$0.0146 \times 3.4 \div 52.6$  equals 0.0009437 or  
1 c.c. KCN solution equals 0.0009437 gm. nickel.

CALCULATIONS FOR COBALT IN COBALT NICKEL STEELS.

Sample 800 mgs.

AgNO <sub>3</sub>	1st titration.		KCN required to clear second cloud which formed after six minutes.
	KCN	2nd titration.	
54.0	0.2	1.0	
<u>56.0</u>	<u>78.4</u>	<u>5.7</u>	
2.0	78.2	4.7	
	<u>4.7</u>		
	82.9		
	2.2		
	<u>80.7</u>		
	27.6		
	<u>53.1</u>		

Cobalt and nickel required 80.7 c.c. KCN in 0.8 gram of sample. Since 3.26 % nickel was found by separate determination, therefore  $0.0326 \times 0.8 = 0.02608$  gram nickel, which divided by 0.00095 = 27.45, or 27.45 c.c. of KCN to be deducted from the total, or 80.7 c.c. This gives 80.7 - 27.45, or 53.25 c.c. of KCN used by cobalt alone.  $53.25 \times 0.00068 \times 100 \div 0.8 = 4.52$  per cent Co.

Sample 1 gm.

AgNO <sub>3</sub>	1st titration.		KCN required to clear the second cloud which forms after six minutes.
	KCN	2nd titration.	
56.0	0.6	57.0	
<u>58.0</u>	<u>99.0</u>	<u>62.2</u>	
2.0	98.4	5.2	
	<u>5.2</u>		
	103.4		
	2.2		
	<u>101.2</u>		
	34.3		
	<u>66.9</u>		

Cobalt and nickel required 101.2 c.c. of KCN for 1 gm. sample. Since 3.26 per cent nickel was found by separate determination, therefore  $0.0326 \times 1.0 \div 0.00095 = 34.31$ .  $101.2 - 34.3 = 66.9$  or KCN used by cobalt alone.  $66.9 \times 0.00068 \div 1 \times 100 = 4.55$  per cent cobalt.

### THE DETERMINATION OF SMALL AMOUNTS OF NICKEL IN THE PRESENCE OF LARGE PER CENTS OF COBALT.

Dissolve 1 or more grams of the cobalt in 40 c.c. of 1.20 nitric acid; add 15 c.c. of 1 : 3 H<sub>2</sub>SO<sub>4</sub>; boil off nitrous fumes; cool; add 5 grams of citric acid per gram of cobalt taken; add a slight excess of ammonia. Cool and add 20 c.c. of a 2 per cent solution of the dimethylglyoxime in 95 per cent alcohol for every gram of metallic *cobalt* present. Let the cold solution stand for at least one hour; filter out the precipitate of the nickel compound which owing to contamination with Co may not have its true scarlet color. It is washed with "dimethyl" wash consisting of 10 c.c. of the dimethyl solution diluted with 500 c.c. of water, and is redissolved in 25 c.c. of 1.20 nitric acid, and reprecipitated as before. The now scarlet precipitate is washed as at first; dissolved; 15 c.c. of 1 : 3 sulphuric acid are added to the solution which is then boiled 15 minutes. 5 grams of citric acid are added and the nickel is titrated with cyanide and "silver" as in steels. This method should answer for the separation of small amounts of nickel from large amounts of elements, like manganese and chromium, which give very dark fluids when held in ammoniacal solution by ammonium citrate. In this way large weights of these elements could be taken as in the case of the Co.

### THE TESTING OF NICKEL FOR SMALL AMOUNTS OF COBALT.

Dissolve 4 or 5 grams of the nickel millings in 1.20 nitric acid, using 10 c.c. of the acid for every gram of the sample taken. Boil off the red fumes; dilute to 20 c.c.; add ammonia until a slight precipitate forms that does not dissolve on long stirring, if iron or aluminum be present; if neither of these elements are in the solution then add the ammonia until a piece of litmus paper floating in the solution just turns blue. Now add acetic acid (1 part of glacial acetic acid diluted with an equal volume of water) until the precipitate just dissolves, or the litmus turns to red, or the solution smells of a slight excess of acetic acid; add an

excess of 10 c.c. of the acetic acid; dilute the solution to 400 c.c. and add 25 grams of potassium nitrite when, after a few minutes, the solution will begin to cloud with a precipitate of the tri-potassium cobaltic nitrite. If the percentage of Co present is very small, being less than 0.1 per cent, then the precipitate will appear yellow only after the lapse of an hour or two. If there be from 0.3 to 0.5 per cent of Co in the sample then the cobalt will quickly form in a bright yellow powder, and slowly settle to the bottom of the beaker. After standing 12 hours the precipitate is filtered off and washed with 25 grams of potassium nitrite dissolved in 300 c.c. of water and made slightly acid with acetic acid. The precipitate should be mixed with some finely divided filter pulp before filtering. Wash it until the washings no longer give any color with a solution of dimethylglyoxime.

The yellow precipitate is then dissolved in 40 c.c. of hot 1 : 1 HNO<sub>3</sub>, and the filter is thoroughly washed with the acid. The filtrate and washings are made slightly ammoniacal and 20 c.c. of "dimethyl" are added to each test. This gives a brown color whose depth is proportional to the cobalt present and is compared with known amounts of cobalt ammonium sulphate put through all of the above operations. The color is almost exactly the same shade as that obtained in the color carbon test in steels.

If, when the yellow cobalt precipitate is washed with the above nitrite wash, it is found that the nickel is very difficult to remove, the yellow precipitate can be redissolved, reprecipitated and washed again. This treatment should remove the nickel to the extent that the cobaltic-nitrite can be readily washed free of nickel test with the "dimethyl" wash.

The above procedure constitutes a very delicate qualitative test for cobalt in the presence of nickel. Less than 0.100 per cent of Co can be readily detected in 5 grams of nickel. The operator should be careful to carry out either the qualitative or the quantitative precipitation exactly as described for the quantitative method, as there are conditions which cause the cobalt to precipitate very slowly and imperfectly. If, when the nitric

acid solution of the yellow precipitate is made ammoniacal, prior to the addition of the "dimethyl" to obtain the brown color, a precipitate of iron appears, this iron must be removed as iron also gives a color with this reagent. Make a basic acetate separation of the iron, in the usual way, in a volume of 100 c.c. Make a second basic acetate separation of the iron and combine the two filtrates and washings from the basic acetate precipitations; make ammoniacal; add the "dimethyl" and compare with the standard similarly treated, consisting of 0.2 gram of cobalt ammonium sulphate put through all of the above operations.

## ANALYSIS FOUND.

	Per cent.		Per cent.
Cobalt.....	0.600	Silicon.....	0.28
Nickel.....	98.400	Manganese.....	trace
Iron.....	0.60	Copper.....	0.12

## ELECTROLYTIC METHOD FOR COBALT AND NICKEL IN FERRO-COBALT AND IN COBALT POWDER.

The following method is used by one large German concern for the valuation of their product: 20 grams are dissolved in moderately conc. nitric acid. Any insoluble matter is fused with  $\text{KHSO}_4$  and the fusion is dissolved in diluted  $\text{H}_2\text{SO}_4$  (1 : 3), added to the main solution and then all is transferred to a liter volumetric flask, diluted to mark and mixed well by repeatedly inverting the flask. 25 c.c. of this solution are accurately measured from a 50 c.c. burette that has been rinsed three times with some of the liter solution. These 25 c.c. are evaporated to thick fumes with  $\text{H}_2\text{SO}_4$ ; diluted to 350 c.c. with water; and the copper is precipitated with  $\text{H}_2\text{S}$ . The  $\text{Cu}_2\text{S}$  is filtered out and washed with  $\text{H}_2\text{S}$  water containing a drop of  $\text{H}_2\text{SO}_4$  in 500 c.c. The filtrate and washings from the  $\text{Cu}_2\text{S}$  are evaporated low, in a casserole; 5 c.c. conc.  $\text{HNO}_3$  are added and 75 c.c. of conc.  $\text{HCl}$ ; heated with lid on until all red fumes are gone; the lid is removed and evaporation to 10 c.c. follows. Dilute to 350 c.c.; make a double basic acetate separation of the iron as in

gravimetric method; add 2 c.c. of acetate per 100 mgs. of cobalt present; filter off any iron acetate, wash with acetate water. To filtrate and washings add 35 c.c.  $H_2SO_4$  of 30 degrees Bé and evaporate to fumes; take up with water and add 2 grams of sodium sulphite, also about 40 c.c. of ammonia of about 0.96 sp. gr. The strongly ammoniacal solution should now be about 100 c.c. volume. Electrolyze this solution in the cold with a current of 0.3 to 0.4 amp. and 6 volts for about 6 hours, using a platinum spiral and a gauze electrode of platinum. Weigh as cobalt plus nickel.

#### DETERMINATION OF THE NICKEL.

100 c.c. of the liter solution are neutralized with KOH and KCN is added until the precipitate that forms is dissolved. Add an excess of KOH; add bromine water until a yellow color is obtained; and allow the precipitate to settle for 1 hour. The black precipitate of nickel oxide which still contains a little cobalt is filtered, washed with KOH water and redissolved in HCl containing bromine water. This Ni is then reprecipitated as before, redissolved and the solution is electrolyzed for nickel as in the case of the Co. The nickel is then dissolved off the electrode with  $HNO_3$ . The nitric solution can be titrated with KCN.

The German method precipitates the solution of the deposited nickel with a 1 per cent alcoholic solution of dimethylglyoxime at 50° C. in excess of ammonia. Dry the precipitate to constant weight at 120 degrees. The nickel is then deducted from the cobalt plus nickel determined from the 25 c.c. by electrolysis, and the cobalt obtained by difference.

#### THE METHOD GIVEN IN DETAIL FOR THE DETERMINATION OF COBALT AND NICKEL BY ELECTROLYSIS AS USED BY THE AUTHOR.

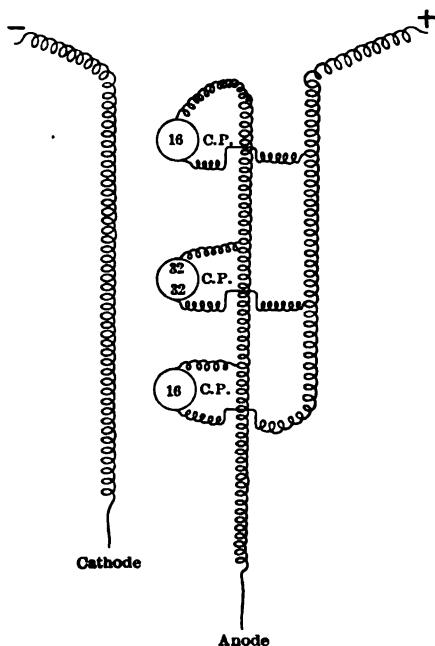
For cobalt powder, cube or ferro-cobalt containing 70 per cent or more of Co, dissolve 0.2 gram (and 0.3 gram for a check) in 35 c.c. of 1 : 3 sulphuric acid, using 600 c.c. beakers. When the

action is over, oxidize any iron by the addition of 10 c.c. of 1.20 nitric acid; boil down to 15 c.c.; add 50 c.c. of water and boil again to 15 c.c.; cool; make the basic acetate separation of the iron in the same way as described under ferro-manganese, page 188. Add 2 c.c. of the slightly ammoniacal ammonium acetate solution for each 100 mgs. of cobalt present. Filter out the acetate of iron; redissolve it and repeat the basic acetate separation. The combined filtrates from the two basic acetate separations are acidulated with 10 c.c. of  $H_2SO_4$  and evaporated to 200 c.c. Ammonia is added until the solution takes on the faintest excess of ammonia. Then 100 c.c. more of 1 : 1 ammonia are dropped in and 2 grams of sodium sulphite. The solutions are transferred to 400 c.c. beakers and electrolyzed with a current of 0.45 ampere and 3.2 volts until the pinkish solution is entirely colorless. The electrolysis is conducted in pairs. The current is turned on and allowed to run all night.

The beakers are arranged so that they can be *lowered* away from the electrodes when the deposition of the cobalt is completed. The electrodes are rinsed off with distilled water; and another beaker is slipped under them and raised and lowered with the electrodes dipping in the water; a second and third beaker of water are also used to wash the electrodes as many more times. The cathode is then dried in an air bath at 100°C. for 45 minutes; cooled; and weighed. It is again washed; dried cooled; and weighed. The final weight less the weight of the cathode, taken before the analysis, equals the weight of the cobalt, and any nickel present. The author has found nickel from traces to 3%, in every case thus far, of cobalt of commerce.

The sketch No. 22 shows an arrangement of electric lamps whereby the amperage can be varied from 0.225 to 0.9 ampere, and from which, with a 220 volt circuit, an electromotive force of 3.2 volts can be obtained. At the points marked 16 c.p., 16 candle power lamps are placed in the circuit. A 32 candle power lamp is put in the socket so marked. With one 16 c.p. lamp burning the current is 0.225 ampere; with two such in action

the amperage is 0.45 and so on. With the 32 lamp the current is 0.45. With all three lamps the amperage is the sum total, or 0.9. The voltage on the main is 220. This group of lights can be arranged on a board 8 by 10 inches. One such group is of course needed for each determination. To determine which is anode and which is cathode, close the switch, wet a piece of tur-



SKETCH No. 22.

meric paper and touch the ends marked "anode" and "cathode" to the paper, when the end which is cathode, or negative, will stain the turmeric red.

The solution from which the Co and Ni have been deposited, is saturated with  $H_2S$ , and any small amount of black sulphide that separates out is filtered out; washed with  $H_2S$  water; ignited in a porcelain crucible at a low red heat; weighed as  $CoO$ ; multiplied by the factor 0.7866 to convert it to the equivalent

of metallic Co; and added to the total of Co plus nickel found on the cathode. The cathode is then placed in hydrochloric acid, which quickly dissolves off the Co and Ni. The cathode is removed and rinsed thoroughly. To the solution and rinsings are added the solution of the small amount of the oxide which has meanwhile been dissolved in a little aqua regia. Make the total solution ammoniacal and precipitate the nickel out of the hot solution with 20 c.c. of the 2 per cent solution of dimethylglyoxime in alcohol. The red precipitate is dissolved in nitric acid; reprecipitated as before; washed with dilute nitric acid water; and finished by the ordinary titration with KCN and silver nitrate. The milligrams of metallic nickel so found are deducted from the total of Co and Ni found by the electrolysis plus any recovered by H<sub>2</sub>S, giving the cobalt by difference. If the operator wishes to guard against the presence of copper, H<sub>2</sub>S should be passed through the solution of the total cobalt plus nickel before adding the dimethyl. Any sulphides so precipitated are filtered out; washed and titrated with KCN for copper as in steels. The filtrate and washings from the copper are evaporated low; oxidized with nitric acid; and then the nickel is obtained with the dimethyl, as described. If the operator wishes, the nickel can be gotten on a separate portion as described under the determination of nickel in metallic cobalt.

The cylindrical cathode and disc anode of platinum are the most convenient form of electrodes for this work. One can use also a platinum dish for the cathode, suspending in the fluid in the dish any convenient form of platinum anode.

*Phosphorus, sulphur and silicon* can be determined in metallic cobalt as in plain carbon steel. In all of the samples that the author has analyzed, at least, very accurate results for sulphur were obtained by the ordinary evolution method. These results were checked by gravimetric results obtained by the same method as recommended for sulphur in tungsten powder by fusing with a mixture of sodium carbonate and sodium peroxide. See page 73.

**MANGANESE IN HIGH PERCENTAGE COBALT STEEL AND  
METALLIC COBALT.**

Dissolve 0.100 and 0.05 gram of steel, cobalt powder, or ferro-cobalt in 20 c.c. of conc. HCl diluted with 10 c.c. water. Dilute to 50 c.c. and neutralize with ammonia. Redissolve the hydroxides in glacial acetic acid. Avoid much excess of acetic acid. Dilute to 100 c.c. with water and pass H<sub>2</sub>S in the cold to remove the main portion of the cobalt. Filter off cobalt sulphide, wash it 50 times with H<sub>2</sub>S water, evaporate filtrate and washings in a casserole to 20 c.c.; cool; add 100 c.c. conc. nitric acid; heat with cover on until all red fumes are gone; remove cover and evaporate to 25 c.c. Dilute to 50 c.c. with water and evaporate again to 25 c.c. Transfer to 10 by 1 inch test tubes and finish as in plain carbon steel. The bulk of the cobalt is removed only because it gives such a strong pink in nitric solution that the operator cannot get an end point when titrating with arsenious acid as in steels. Steels containing 5 per cent Co do not interfere in this way, but if the percentage of Co runs much higher, the cobalt must be removed before titration.

Cobalt steels containing much chromium and tungsten should be dissolved in 20 c.c. of 1 : 3 H<sub>2</sub>SO<sub>4</sub> and oxidized with 15 c.c. 1 : 20 nitric acid; boil down to 10 c.c.; filter off tungsten; wash with dilute H<sub>2</sub>SO<sub>4</sub>; neutralize with ammonia; acidulate with acetic acid and proceed as above. This removal of cobalt is only necessary in very high percentages, at least 10 per cent cobalt.

**ANALYSES OF METALLIC COBALT AND FERRO-COBALT.**

	Per cent Co	Per cent Ni	Per cent Fe	Per cent Al	Per cent Si	Per cent S	Per cent Mn	Per cent P
Bar cobalt.....	94.40	2.59	1.25	1.17	0.31	0.031	0.21	0.016
Lump cobalt.....	98.56	0.80	0.48	.....	0.30	0.017	0.20	0.017
Powder.....	96.61	1.87	0.70	.....	0.26	0.157	0.26	0.012
Cubes.....	97.56	2.10	0.35	.....	0.08	0.022	0.08	0.022
Ferro-cobalt.....	75.25	0.60	21.49	1.90	0.77	0.014	0.08	0.019

When neutralizing with ammonia, prior to adding the excess of acetic acid, do not completely precipitate the iron, etc., but just add enough ammonia to produce a slight permanent precipitate. Then redissolve the latter in acetic acid as directed.

**Stellite.** Cobalt, Molybdenum, Iron, Manganese, Chromium.

Dissolve 1 gram and 800 mgs. in 30 c.c. conc. HCl and 30 c.c. conc. nitric acid; evaporate to 20 c.c.; add 100 c.c. conc. nitric acid and evaporate to dryness, but do not ignite, as cobalt may become insoluble. Dissolve in 50 c.c. conc. HCl; evaporate to 20 c.c.; transfer to 1000 c.c. boiling flask; and dilute to 200 c.c. Peroxidize; add  $\text{Na}_2\text{O}_2$  until black precipitate forms and tends to settle; add 10 grams more of peroxide and 10 grams  $\text{Na}_2\text{CO}_3$ ; bring just to boil; continue to boil 10 minutes; cool; filter on double 15 cm. papers and wash with peroxide water.

Redissolve the black precipitate in 60 c.c. 1 : 1 HCl; and preoxidize again as before and so on until filtrates are free of yellow color. Three peroxidations are sufficient. Residue on filter is cobalt and iron. Dissolve off filter as before; filters are washed. Ash the filters and extract any remaining cobalt with 10 c.c. HCl and add to main cobalt and iron solution. Two basic acetate separations are made of this solution as in cobalt steel. Then finish filtrates by phosphate precipitation as in cobalt steels. The acetate of iron on the filter can be dissolved in HCl, reprecipitated and weighed; or titrated as in iron ore.

Chromium is obtained as in chromium ore, except that the iron and cobalt are filtered out and washed with sodium peroxide wash. Filtrate and washings are boiled for 20 minutes to remove  $\text{H}_2\text{O}_2$  and titrated with ferrous ammonium sulphate as in chrome ore.

Molybdenum is gotten from a separate portion, dissolving in the same mixture as in cobalt steel. The molybdenum is then precipitated as in steel with  $\text{H}_2\text{S}$ .

Manganese is determined as in cobalt steel, removing most of the cobalt with  $\text{H}_2\text{S}$ .

Silicon is found by fuming with sulphuric acid, as in chrome steel.

## ANALYSIS OF STELLITE.

	Per cent.		Per cent.
Cobalt.....	60.80	Iron.....	.6.52
Molybdenum.....	24.10	Silicon.....	.0.27
Chromium.....	13.20	Phosphorus.....	.0.02
Manganese.....	0.55		

OXYGEN AND SALTS (SODIUM CHLORIDE, ETC.) IN  
METALLIC COBALT.

*The oxygen* is determined on the finely powdered sample as in tungsten (see page 74).

*Salts other than cobalt salts* are determined by extracting the finely divided sample by boiling it in distilled water in a platinum dish until the decanted extract no longer leaves a residue on evaporation. The extract is decanted through a filter. The combined extracts are dried at 120° C. and weighed. The extract is then dissolved in water and a little HCl, if necessary; made very faintly ammoniacal and saturated with H<sub>2</sub>S. Any precipitate so obtained is filtered out; washed with H<sub>2</sub>S water; ignited in a porcelain crucible; weighed; and deducted from the weight of the extract dried at 120° C. The following is an analysis of an alleged c.p. metallic cobalt powder; Co, 95.45 per cent; Si, 0.01 per cent; C, 0.25 per cent; chlorides, other than cobalt salts, 1.89 per cent; O, 1.72 per cent.

## CHAPTER XV.

### PART I.

#### THE DETERMINATION OF NITROGEN IN STEEL AND IRON.

A NUMBER of English and American chemists prefer to determine the nitrogen in steel by dissolving it in 1 : 1 HCl. The nitrogen is supposed to exist in the steel as  $\text{Fe}_5\text{N}_2$  or  $\text{Fe}_4\text{N}_2$  and is converted into ammonia by evolved hydrogen. This ammonia then combines with the HCl to form ammonium chloride. This solution of iron chloride and ammonium chloride is poured into a flask of the style shown on page 269 but of 700 to 750 c.c. capacity. A double bored stopper is used in the flask. Through one hole is passed a long stemmed separatory funnel whose tube just dips under the fluid in the flask when all of the solutions are in it. The other hole in the stopper is for a glass delivery tube, one end of which just passes through the stopper into the flask and the other end is connected with a glass condenser of the Liebig type. Before introducing the solution of the sample, 12 grams of NaOH in 250 c.c. of water are put in the flask; the latter is connected with the condenser; and about half of the water is distilled off to remove any nitrogen that may be in the NaOH before the actual determination of that in the sample is begun.

Having purified the NaOH from any nitrogen it may contain, as above, the 1 gram of sample which has meanwhile been dissolved in 20 c.c. of 1 : 1 HCl is run slowly into the flask (which is first connected with the condenser) via the separatory funnel. When all of the solution of the steel is in the flask, it is given a whirling motion to mix thoroughly the HCl solution of the steel with the NaOH. The mixture is then brought to a boil, and the boiling is continued until the distillate which is received in Nessler tubes no longer gives the

characteristic brown color with Nessler solution.\* The total distillate is then treated with 2 c.c. of the Nessler reagent per each 200 c.c. of distillate. The brown colored solution so obtained is then matched against standard ammonium chloride which is made by dissolving 0.0382 gram of this salt in one liter volume of water. As ammonium chloride contains 26.18 per cent of nitrogen,  $0.0382 \times 0.2618$  equals 0.010 gram of nitrogen, hence 1 c.c. of the above standard is equivalent to 0.0001 gram of nitrogen.

The most convenient way to make this comparison is as follows: Suppose that 200 c.c. of the distillate were obtained. This would then be treated with 2 c.c. of the Nessler solution and well mixed in a Nessler tube or other convenient comparison tube. Then place 200 c.c. of water in a duplicate comparison tube together with 2 c.c. of the Nessler solution. Next drop from a burette, with constant mixing, into this Nessler solution and water, some of the standard ammonium chloride until the color of this mixture just matches that of the distillate. Suppose that the reading of the burette showed that it required an addition of 35 c.c. of the ammonium chloride standard to produce in the imitation mixture a depth of color equal to that of the distillate obtained from the steel; this gives the volume of the test as 202 c.c. and that of the standard as 237 c.c. As 35 c.c. of the standard solution of ammonium chloride were required then the distillate must contain  $0.00035 \times 202 + 237 \times 100 \div 1$  or 0.029 per cent nitrogen. A blank determination must be run including all of the chemicals and operations, and any nitrogen so obtained must be deducted from that found in the steel. The accuracy of the manipulations can also be tested by putting a measured amount of the ammonium chloride standard solution through all of the operations, and any nitrogen found in excess of that added in the form of ammonium chloride should equal the blank determination.

Ledebur prefers to determine nitrogen in iron or steel by dis-

\* The reaction causing the brown coloration is explained by the following equation:  $2(2\text{KI}, \text{HgI}_2) + \text{NH}_3 + 3\text{KOH} = \text{NHg}_2\text{IH}_2\text{O} + 7\text{KI} + 2\text{H}_2\text{O}$ .

solving 10 grams of the sample in a flask similar to the one used in the foregoing method, using 120 c.c. of dilute sulphuric acid made by diluting 1 part of conc. sulphuric acid with 4 parts of water. When the sample is entirely dissolved, the flask *A*, Fig. 23, is connected to a duplicate flask *E* containing a little water. This second flask is in turn connected with a nitrogen bulb *F* approximating very closely to the Volhard nitrogen bulb. The Volhard bulb has a stopper through which the delivery tube from the second flask containing a little distilled water passes. This delivery tube dips almost to the bottom of the nitrogen bulb in which is placed exactly 25 c.c. of N/10 sulphuric acid. 100 c.c. of water containing 40 grams of NaOH are poured through the separatory funnel into the solution of the steel in *A*. The mixture of hydroxide of iron and NaOH is boiled gently and at the same time a stream of air is drawn through the entire apparatus. The boiling and drawing of air is continued for an hour. By this time all of the ammonium sulphate formed from the nitrogen in the steel is supposed to have been converted into ammonia by the action of the NaOH and been drawn over into the N/10 sulphuric acid in the nitrogen bulb. The contents of the latter are then titrated with N/10 NaOH with a few drops of methyl orange for an indicator. The number of c.c. of the N/10 sulphuric acid found by this titration to have been neutralized by the ammonia coming from the nitrogen in the steel, is multiplied by the factor 0.001401 to find the part of a gram of nitrogen that existed in the 10 grams of steel. This method is to be commended by reason of the fact that a large sample can be taken, and it is not dependent on the operator's skill in matching colors.

#### CALCULATIONS.

The factor 1 c.c. of N/10 sulphuric acid equals 0.001401 gram of nitrogen is obtained as follows: Since 1 c.c. of N/10 sulphuric acid contains 0.0049038 gram of H<sub>2</sub>SO<sub>4</sub>, and this acid unites with ammonium hydroxide according to the equation H<sub>2</sub>SO<sub>4</sub> + 2 NH<sub>4</sub>OH = (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + 2 H<sub>2</sub>O, we have the proportion given below:



or



or

$$X = 0.0014009 \text{ gram of nitrogen.}$$

Suppose it is found by titration of the 25 c.c. of  $\text{H}_2\text{SO}_4$ , after the absorption of the ammonia formed from the nitrogen in the steel, that only 23 c.c. of the N/10 NaOH are required to discharge the pink color given to the 25 c.c. of the N/10  $\text{H}_2\text{SO}_4$  by the methyl orange. This would mean that 25 c.c. less 23 c.c. or 2 c.c. of the N/10 sulphuric acid had been neutralized by the ammonium hydroxide coming from the nitrogen in the steel and the blank. If there were no deduction for a blank then the percentage of nitrogen found would be  $0.001401 \times 2 \times 100$  divided by 10 or 0.028 per cent nitrogen.

#### NESSLER SOLUTION.

35 grams of potassium iodide are dissolved in 200 c.c. of distilled water. To this KI is added a saturated solution of mercuric chloride until a faint precipitate is obtained. Next add 160 grams of potassium hydroxide. Dilute to one liter and add more of the mercuric chloride solution until a small permanent precipitate of mercuric iodide forms and remains. This precipitate on settling should leave a pale yellow supernatent fluid which is supposed to become more sensitive with age. It gives a brownish yellow tint to small traces of ammonium or its salts in solution. If large quantities of ammonia are in solution the Nessler reagent produces a precipitate.

According to Braune when the nitrogen reaches 0.035 per cent in the high carbon steels it causes serious brittleness.

It is very necessary in making nitrogen determinations to carry out the work in a room free from all ammonia fumes. The work should be done in a place apart from the other laboratory work. In drawing air through the train in the method described

by Ledebur it would seem advisable to purify such air by passing it through a wash bottle containing some dilute sulphuric acid, before it enters the boiling flask.

## APPARATUS OF LEDEBUR FOR THE DETERMINATION OF NITROGEN IN STEEL.

In his *Leitfaden für Eisenhütten-Laboratorien*, Ledebur uses the apparatus shown in Fig. 23. The steel is dissolved in *A* and

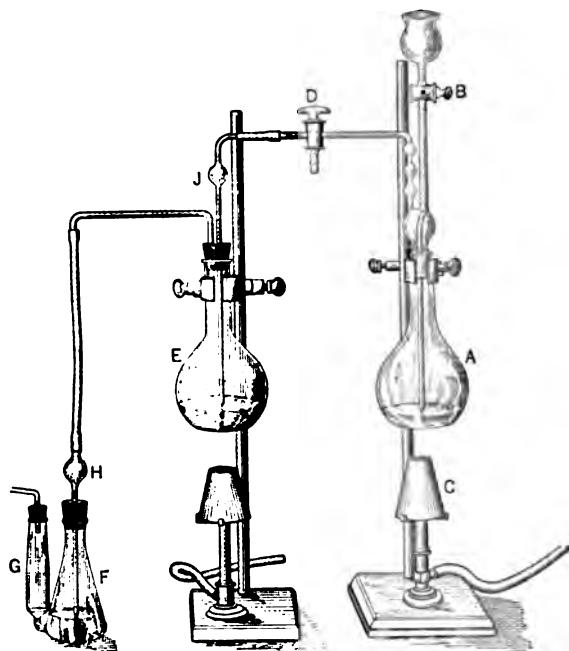


FIG. 23.

the NaOH is introduced through *B*. The air is drawn through *A* and *E*, carrying the ammonia formed from the nitrogen in the steel through *E* over into the measured amount of N/10 sulphuric acid in *F* where it is absorbed and determined as already described.

## CHAPTER XVI.

### THE ANALYSIS OF GRAPHITE AND GRAPHITE CRUCIBLES.

THE total carbon is determined by direct combustion in the electric furnace. The sample is reduced to sufficient fineness to pass through No. 11 bolting cloth. A hardened steel mortar is used with a ball pestle. The chamber of the mortar is  $3\frac{1}{2}$  inches deep by  $1\frac{3}{4}$  inches in diameter. The total thickness of the steel block is 4 inches. The pestle fits, exactly, the bottom of the mortar. The material is pounded into this opening by striking on the end of the pestle with a hammer. It is then taken out and ground in an agate mortar to loosen the mass which is sifted through the bolting cloth. The portion that does not pass the cloth is put back into the steel mortar and hammered again, and so on until the sample all passes through the cloth.

0.200 to 0.300 gram of sample is used, and it burns completely in oxygen in the electric furnace. Forty-five minutes elapse from the time the sample is put in the furnace until the absorption apparatus is detached for the final weighing of the carbon dioxide formed. The weight of the  $\text{CO}_2$  multiplied by 27.27 and divided by the weight taken for analysis yields the exact carbon in the sample.

### VOLATILE MATTER.

One gram of sample is burned in a platinum crucible with a slow stream of oxygen passing in through a hole in the lid of the same. The lid is removed and the contents stirred with a nickel wire at intervals of about twenty minutes. The porcelain tube of a Rose crucible is used to conduct the oxygen through the hole in the platinum lid. When the contents of the crucible no longer lose weight the ignition is stopped. The total loss

of weight less the weight of carbon by combustion equals the volatile matter other than carbon, such as water and sulphur.

A direct determination of water can also be made by igniting the substance in a stream of air, dried by passing it through a jar of phosphoric anhydride such as is used in the carbon combustion train. (See Fig. 7 (*J*), page 211.) The sample is put in a clay boat and heated to redness in a porcelain or quartz combustion tube.\* In the outlet end of the tube is attached, by means of a rubber stopper and glass tube, an absorption jar containing phosphoric acid. The outlet of the absorption jar is guarded against the ingress of moisture by a calcium chloride tube closely filled with bits of stick caustic potash. The air is drawn through by a suction pump. At intervals of twenty minutes the heat is lowered, the passing of the air is stopped and the absorption jar is weighed. It is attached again, the heat raised to redness for another twenty minutes, and the weighing is again made as before, and so on until there is no more gain than is obtained by a blank test carried through in the same manner. The total increase in weight of the phosphoric anhydride less the blank is calculated to percentage as water.

A blast lamp flame is used to expel the carbon, obtain the ignition loss, and the ash for analysis. The ash from the 1 gram taken for ignition loss is analyzed for its various constituents exactly as a clay. It is fused with a mixture of 10 grams of anhydrous carbonate of soda plus one gram of niter in a platinum crucible. The melt is dissolved out with water in a platinum dish, using heat to hasten the solution. The water extraction is transferred to a No. 6 porcelain dish. The dish is covered with a watch glass, and 1 : 3 sulphuric acid is allowed to flow down the under side of the lid until 125 c.c. in all have been slowly added. The acidulated fusion is stirred cautiously with a glass rod extending under the cover. The solution is heated until all effervescence is over. The under side of the

\* The apparatus shown in photo No. 1, page 75, or Fig. 1 on page 77, omitting the pyrogallic solution, and passing air or oxygen through the apparatus instead of hydrogen, can be used for this determination.

cover is rinsed off, the washings flowing into the dish. The contents of the latter are then evaporated to thick fumes of sulphuric anhydride. Cool. Add enough water to dissolve the sulphates, heating for about twenty minutes. Cool again. Add paper pulp. Filter and wash with 1 : 10 sulphuric acid. Wash 60 times, allowing each washing to drain off before the next one is added. The residue on the filter is burned at lowest possible heat until pure white. The heat is then raised to blast for ten minutes. The crucible is cooled in a desiccator and weighed. The contents are blasted again, or until no further loss occurs. A few drops of sulphuric acid are added, the crucible is filled to about two-thirds its capacity with hydrofluoric acid and evaporation in a good draft to fumes of sulphuric acid follows. The sulphuric acid is driven off, the crucible is heated to bright red and weighed again. The loss of weight is the silica, which multiplied by 100 and divided by the weight taken yields the percentage of the latter oxide.\*

The filtrate from the silica is reduced with 10 grams of zinc and titrated for iron with potassium permanganate to first pink that lasts for a few seconds. The iron is calculated to oxide.

If alumina is also wanted, the filtrate from the silica is first precipitated in a No. 7 porcelain dish in about a 600 c.c. volume with the faintest possible excess of ammonia water which has been filtered free of any sediment or scales of glass. When the solution is faintly ammoniacal it is boiled, cooled, and ashless paper pulp added in sufficient quantity to secure rapid filtration and washing. The aluminum and iron hydroxides are washed free from sulphates with ammonium nitrate water. The washings are tested with barium chloride, and when no milkiness forms in the former on addition of the chloride, the precipitate is given ten more washings. The filter and precipitate are burned cautiously in a weighed platinum crucible after first

\* There may remain in the crucible, after the evaporation with HFL and  $H_2SO_4$ , and the ignition, a little stain of iron which should be dissolved in a little HCl, evaporated to thick fumes with a few drops of  $H_2SO_4$ , and added to the filtrate from the silica before the reduction of the iron.

drying out some of the excessive amount of water held by the pulp. The paper pulp is roasted out and the ash ignited to a constant weight with a blast lamp. The precipitate is calculated as alumina plus oxide of iron. All of the phosphorus present in the graphite will be counted as alumina unless it is desired to separate it. In that event the solution should be divided before the ammonia precipitation is made. Pour it into a 500 c.c. flask. Dilute to the 500 c.c. mark with water. Mix the contents thoroughly and pour enough of the latter into a 250 c.c. flask to fill it to the mark.

This gives two portions; one is reduced at once with zinc and titrated with permanganate for iron. The permanganate standard is made by dissolving 0.727 gram of potassium permanganate in water and diluting it to 1000 c.c. 1 c.c. of this standard equals 0.001284 gram of iron. In a burned pot the iron is calculated to ferric oxide. Therefore the iron found in parts of a gram is multiplied by 10 and divided by 7 to obtain the amount of ferric oxide. It is necessary to make this calculation in all cases where alumina is asked for. In plumbago, or graphite, it is usually customary to calculate the iron to protoxide ( $\text{FeO}$ ). To obtain the amount of the latter, multiply the weight of metallic iron found by  $\frac{9}{7}$ . These weights of oxide are then reduced to percentage in the usual way.

#### PHOSPHORUS AND ALUMINA.

The other 250 c.c. portion of the divided sulphate filtrate is precipitated with a faint excess of ammonia, washed, roasted, and blasted to constant weight as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ . The ferric oxide found in the 250 c.c. reduced with zinc is deducted from the total weight of the three oxides found in the second portion. This leaves  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ . The phosphorus is obtained by fusing the oxides with twenty times their total weight of sodium carbonate plus four times their weight of potassium nitrate. The melt is dissolved in a few c.c. of water, filtered into a 5-ounce beaker, washing the filter thoroughly with ammonium nitrate water. The filtrate is acidulated with 1.20 nitric acid, boiled with

a slight excess of permanganate solution (see Phosphorus in Steel), and the phosphorus is finished as in steel. The phosphorus obtained is calculated to the pentoxide ( $P_2O_5$ ) as follows: For example, suppose 10 c.c. of the alkali standard were used, then  $10 \times 0.0001 \times 1.63$  equals 0.00163, which multiplied by  $\frac{71}{81}$  equals the phosphorus pentoxide to be deducted from the weight of  $Al_2O_3$ ,  $P_2O_5$ . This leaves the alumina which came from the 0.500 gram of sample. It is reduced to percentage by the usual calculation. If phosphorus is not asked for, it is unnecessary to divide the sulphate filtrate from the silica. It can be precipitated with ammonia, filtered, washed, roasted, ignited, and weighed as  $Al_2O_3$ ,  $Fe_2O_3$ , ignoring the presence of phosphorus, which is not likely to introduce a serious error. The total oxides are then fused with 10 grams of sodium carbonate, the melt dissolved in excess of 1 : 3 sulphuric acid (about 85 c.c. of the acid); reduced with zinc and titrated with permanganate. The iron is calculated to  $Fe_2O_3$  and deducted from the  $Al_2O_3$  and  $Fe_2O_3$  to obtain alumina.

#### LIME AND MAGNESIA.

If lime and magnesia are asked for, the ash from the graphite is fused as before, but is acidulated with an excess of hydrochloric acid instead of sulphuric acid.

The silica is removed by evaporating twice to hard dryness and filtering between evaporation. It is washed with 1 : 10 hydrochloric acid. The filtrate and washings are precipitated with a slight excess of ammonia that has been freed from carbon dioxide as follows: The ammonia water is put in a sulphur flask fitted with a No. 6 stopper through which passes a glass tube. This tube is connected by rubber tubing with a jar such as shown in Fig. 4, page 209, filled with short pieces of stick caustic potash. The connection is with the top of the jar. The ammonia water in the flask is heated by a Bunsen burner. This drives the concentrated ammonia from the flask over into the jar of caustic potash, which removes the  $CO_2$ . The purified ammonia passes out at the bottom, and from thence via

more rubber tubing it reaches the glass delivery tube, which dips into a reagent bottle containing distilled water that has been boiled for half an hour and cooled without stirring. The ammonia is passed into this bottle until the water in it smells strongly of ammonia. The carbondioxide-free ammonia is used for all separations of iron from lime.

The filtrate from the iron and alumina is concentrated to 300 c.c. and made faintly ammoniacal. If the presence of manganese is suspected, a slight excess of bromine is added, and the solution is heated until the brown flakes of manganese separate. This is not done unless the carbonate and nitrate fusion of the original ash is noticeably green.

The hot faintly alkaline filtrate is treated with 20 c.c. of saturated solution of ammonium oxalate to precipitate the calcium as oxalate. The latter is permitted to settle several hours. It is then filtered out and washed with hot water containing a little ammonium oxalate, until free of chlorine test with silver nitrate solution.\* The precipitate is roasted until white and blasted to constant weight. It is weighed as calcium oxide, which is calculated, as such, to percentage. The filtrate from the lime is acidulated with HCl, concentrated to a small volume; filtered; made slightly ammoniacal; cooled; 10 c.c. of saturated solution of microcosmic salt are added; and then the total volume is increased one-fourth with concentrated ammonia. After thorough stirring, the precipitate of ammonium magnesium phosphate is permitted to settle until the next day. It is filtered on a small filter and washed forty times with a mixture of one part of conc. ammonia and three parts of water. It is then burned at a low red heat until white, and weighed as magnesium pyro-phosphate, which contains 36.21 per cent magnesium oxide.

The filtrate and washings should be treated with more phosphate solution, and, if an appreciable precipitate forms, it is collected, washed, ignited, weighed and added to the principal residue.

\* Acidulate the washings with a few drops of 1.20 nitric acid before testing for chlorine.

## SILICON CARBIDE.

When complete analyses of old pots that present a green-colored fracture are made, the analytical data will give evidence of the presence of silicon existing in the reduced state, that is not entirely as oxide. If the silica, alumina, iron oxide and lime obtained are calculated as such and to their sum is added the total carbon as found by the RED LEAD process, the percentages may reach the impossible total of 115.8 per cent in some instances. Such pots when broken present a greenish fracture. When the writer first encountered this difficulty he was somewhat puzzled. Such material cannot be burned free of black or grey residue in a stream of oxygen. This is characteristic of silicon carbide. The combination will not yield its carbon in the electric furnace with oxygen alone. It decarbonizes readily if burned with red lead. For carbon 0.300 gram of green fracture pots is burned with 4 grams of red lead. The blank due to the red lead is deducted, and the carbon percentage calculated as in pots free from silicon carbide. The ignition loss, which, in a burned pot, will ordinarily check within 0.1 to 0.2 per cent of the red lead result, will fall below the total carbon as much as 6 or 7 per cent in the old pots containing the silicon carbide, due to the fact that the carbon cannot be burned out of the silicon carbide except with red lead.

The writer estimated the carbide as follows: The total carbon obtained by red lead combustion and the ignition loss obtained by blasting in a stream of oxygen were both calculated to a 1 gram basis. The weight of carbon by ignition loss was deducted from the weight of the total carbon. The remainder was calculated to silicon carbide. Then the excess of per cents above 100 per cent was assumed to be oxygen. The amount of silicon required to combine with this oxygen was calculated. The silicon was then figured to carbide. The per cent of carbide gotten in this manner checked fairly well with that found by calculating from the difference between the total carbon and the ignition loss. The silicon required to combine with the

silicon carbide found was calculated to silica and deducted from the total silica. The carbon remaining after the ignition in oxygen was deducted from the total carbon. A sample analysis of an actual case is appended.

	Per cent.
Free carbon.....	38.92
Silicon carbide.....	20.14
Iron oxide (FeO).....	4.37
Alumina.....	15.11
Free silica.....	20.47
Lime.....	0.98
	<hr/>
	99.99

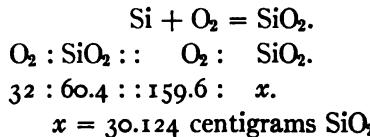
#### *Calculations for Silicon Carbide.*

After having made a number of determinations of silicon carbide in old pots, with green fractures, the author has found it more satisfactory to obtain the total percentage footing of the oxides and carbon. Assuming the excess above 100 per cent to be due to silicon existing as carbide, instead of oxide, the calculations are as follows:

#### ANALYTICAL DATA (EXAMPLE).

	Per cent.
Total carbon.....	44.90
Total "silica" obtained.....	50.60
Alumina.....	15.11
Total iron calculated as protoxide (FeO).....	4.37
Lime.....	.98
Total.....	<hr/> 115.96

**Free Silica.** This gives on a 1 gram basis 159.6 milligrams excess, which is assumed to be oxygen. This is equivalent to 30.12 centigrams of silica:



to be deducted from the total silica, or 50.6 minus 30.124 equals 20.47, or 20.47 per cent free silica in the pot.

**Silicon Carbide.** Silica is reduced to silicon by the factor 0.4702, therefore the 30.124 centigrams of silica correspond to

$30.124 \times 0.4702$  equals 14.16, or 14.16 per cent silicon. This is equivalent to 20.14 centigrams of silicon carbide.

$$\begin{aligned} \text{Si} + \text{C} &= \text{SiC}. \\ \text{Si} : \text{SiC} &:: \text{Si} : \text{SiC}. \\ 28.4 : 40.4 &:: 14.16 : x. \\ x &\text{ equals } 20.14 \text{ or } 20.14, \text{ SiC in the pot.} \end{aligned}$$

**Free Carbon.** The 20.14 centigrams of silicon carbide correspond to 5.98 centigrams of carbon to be deducted from the total carbon found:

$$\begin{aligned} \text{C} + \text{Si} &= \text{SiC}. \\ \text{C} : \text{SiC} &:: \text{C} : \text{SiC}. \\ 12 : 40.4 &:: x : 20.14. \end{aligned}$$

$x$  equals 5.98, or 44.90 minus 5.98 equals 38.92, or per cent of free carbon in the pot.

#### RESULTS.

Excess of Oxygen Calculated to Silicon Carbide.	Excess of Oxygen Calculated to Silicon.
Per cent.	Per cent.
38.92 carbon (free)	44.90 total carbon
20.14 silicon carbide	14.16 silicon
4.37 protoxide of iron	4.37 iron oxide
15.11 alumina	15.11 alumina
0.98 lime	0.98 lime
20.47 silica	20.47 silica
99.99	99.99

#### SULPHUR IN POTS AND GRAPHITES.

Fuse 1 gram of sample with a mixture of 10 grams of sodium carbonate ground intimately with 10 grams of potassium nitrate. Such a mixture must be heated cautiously as it will flash if heated too quickly. When the first action is over, heat until the fusion is completely molten and keep it so with the least possible heat for a half hour.\* Cool; dissolve the melt with

\* With the present high price of platinum it would be advisable to determine the sulphur as in coke. (See page 403.)

water; acidulate with hydrochloric acid in a 600 c.c. casserole. Heat with cover on until all effervescence is over, rinsing same; evaporate to dryness and finish as sulphur in ferro-vanadium of high silicon content. If such a fusion is heated too hot it will boil out of the crucible.

#### STANDARDIZATION OF PERMANGANATE FOR IRON.

Weigh into a small flask 0.062 gram of oxalic acid c.p. Put into this flask 50 c.c. distilled water and 20 c.c. 1 : 3 sulphuric acid. Warm the solution until the crystals are dissolved and titrate it hot. Do not let the solution boil. It will usually require 43.1 c.c. of this permanganate to change the oxalic acid solution to a slight pink. Deduct 0.2 c.c. blank. Therefore 0.062 divided by  $42.9 \times 8$  divided by 9 equals 0.001284 or 1 c.c. of the permanganate solution equals 0.001284 gram of iron. The value of any permanganate solution in terms of oxalic is multiplied by  $\frac{8}{9}$  to obtain its iron value.

For a check, weigh 0.065 gram of oxalic acid. This will require 45.2 c.c. to render it pink. Therefore 0.065 divided by  $45.0 \times 8$  divided by 9 equals 0.001283, or 1 c.c. standard solution equals 0.001283 gram of iron.

0.727 gram of  $\text{KMnO}_4$  is dissolved in 1 liter of water for the above standard.

## CHAPTER XVII.

### PART I.

#### THE ANNEALING OF STEEL.

AFTER several years of experience with the annealing of steel, during which careful records were kept with a Le Chatelier pyrometer, the writer came to certain conclusions as to the proper temperatures for annealing plain carbon steels and alloy steels.

The pyrometer was sent to the bureau of standards for the verification of its readings.

Briefly the results are as follows:

#### ANNEALING TEMPERATURES.

First. Cast steel of all kinds that has *never been reheated* should be first brought to a temperature of 850° C., and held there for one hour. The heat should then be lowered as quickly as possible to 700 to 720° C. and held at that temperature for ten to twelve hours. The pipes can then be drawn and the steel can be cooled as quickly as desired. The fact is, that if the steel is once perfectly annealed, it can be withdrawn from the furnace, thrown into water and it will be as soft as ever. The author took two pieces of steel from the same saw plate and annealed them, one lying on top of the other, until he knew both were perfectly annealed. He then withdrew the pieces from the furnace. One was thrown directly from the annealing furnace into a bucket of cold water while still at the *annealing* heat. The companion piece was cooled in the air. Both pieces were then pulled in the testing machine and registered identically as to tensile strength and elongation, etc. Steel once perfectly annealed can only have its softness impaired by heating above

the annealing range. Rapid cooling of *perfectly* annealed steel has no effect whatever on its softness.

However, if the annealer has lowered the heat before the steel has been entirely annealed, or in other words has not held it long enough within the range of temperature where that particular steel anneals most quickly, he stands a better chance of getting his steel eventually soft enough for the purpose intended by burying it in ashes or lime. He thus, in reality, holds it longer within the range of temperature where steel anneals *slowly*. That is, the steel passes more slowly through the range of *slow* annealing, being the temperatures below 720° C., than if it had *not* been surrounded by more or less non-heat conducting substances.

Second. The author has found that plain carbon steels, no matter whether the carbon be 0.50 per cent or 1.40 per cent, anneal best and most quickly between 700 and 720° C.

This is also true of most chrome-tungsten and chrome-molybdenum steels. It is particularly noticeable in high speed steels, for if one wishes to drill a high speed test he can render it soft enough by annealing it for one hour at 720 degrees, whereas it will require two to three times that length of time to accomplish the same softening at lower ranges.

Third. On the other hand, high manganese and high nickel content lower the annealing heat. Seven per cent nickel steel anneals to the perfectly annealed state of the carbon at 520 to 550° C.\* Again, the writer has succeeded in softening Hadfield's manganese steel so that it could be drilled without dulling a high speed tool at a temperature of 520 to 550 degrees. The specimen of this steel that the writer first experimented with was of the following analysis:

	Per cent.
Carbon.....	1.40
Manganese.....	13.42
Silicon.....	0.043
Phosphorus.....	0.047
Sulphur.....	0.030

\* Read remarks given on page 347 on the annealing temperatures of different alloy steels.

Plates of this steel, before annealing, could not be drilled even with a high speed drill. After 24 hours' annealing a plate was drilled without sharpening the bit and the latter drilled the plate without "screeching." In fact, four holes were made in such a plate without resharpening. These plates were then taken to the planer and machined easily, but they presented the peculiar property of being very brittle. The condition of the carbon by the acid annealing test showed that the carbon had attained almost entirely to the perfectly annealed state.

Fourth. Steel that has been reheated and rolled or hammered need not be heated above  $720^{\circ}$  C.\* However, if the furnace is heated to 850 degrees, for example, and a lot of steel is charged into it, it can be brought to 720 degrees more quickly. The large body of cold steel will absorb its surplus heat.

**Overheated Steel.** If steel ingots are allowed to lie in soaking pits or reheating furnaces at temperatures approximating welding heats for considerable time, the annealer's task will be greatly complicated, as such steel is much harder to bring into the annealed state.† Bad cases of overheating or prolonged soaking at high heats will require two or three times as long to anneal at the regular temperature. There seems to be nothing to do in such cases but to re-anneal until the carbon is finally brought again into the perfectly annealed condition.

Fifth. It is indeed remarkable that plain carbon cast steel as it comes from the mold can be refined from the most coarse crystalline structure ever found in the raw cast steel to a fine silky fracture by *heat alone*, before it is hammered, rolled or forged in any manner. To accomplish this great change it is merely necessary to heat the steel first as it comes from the mold to  $850^{\circ}$  C. for one hour, and then lower the heat to  $720^{\circ}$  C. and hold the steel at this temperature for twelve to fifteen hours. Then lay it out to cool wherever convenient. A complete anneal, as already stated, is secured in this manner.

\* The author has been able to get better anneals on many forged chrome-tungsten steels by first heating the same through for an hour or so at  $850$  to  $900^{\circ}$  C. and then holding at  $720^{\circ}$  C.

† By reason of the very coarsely crystalline structure formed by the excessive heat.

Sixth. Steel that has been heated to 800 to 850° C. and quenched quickly in water or oil will attain the perfectly annealed condition within thirty minutes to one hour's time at a temperature between 620 and 690° C., whether the carbon be 0.50 or 0.90 per cent, that is, a quenched steel anneals at a lower temperature than when unquenched, and in less time.

#### FORMATION OF GRAPHITIC CARBON AND BLACK FRACTURE.

On three different occasions the writer was called upon to investigate the temperature most favorable to the formation of graphitic carbon, or in other words, to ascertain the real cause of its presence. As a result of extended experimental annealing of cold rolled steel the author has come to assign the cause largely to annealing only, within a range of temperature that causes the carbon to assume the uncombined state.

As mentioned, on three different occasions, three different lots of cold rolled steel, coming from different steel works, were subjected to prolonged annealings, and the progress of the formation of the graphitic carbon was noted.

In two lots the cold rolled steel was free from even traces of the graphite at the beginning of the anneals. Anneals were continued in some instances for 100 hours, but most periods did not aggregate over 40 hours. Anneals were interrupted at 8-to 12-hour intervals to make annealing and graphite tests. Further, a 1.30 carbon tool steel *ingot* was put in a lathe and turned down until there was nothing left of it but a  $\frac{1}{8}$  inch rod. By prolonged annealing between the range of 660 to 700 degrees black fracture was produced. This was raw cast steel that had never been hammered or rolled or forged in any way. The conclusions are as follows:

First. The higher percentages of carbon yield the black fracture most quickly, the range from 1.20 per cent carbon and above being the most favorable. Percentages under 1.00 per cent carbon are perhaps free from appreciable amounts of graphitic carbon, at least under any conditions likely to be met with in practice.

Second. The temperature most favorable to the quick formation of graphite lies between 660 and 700° C.

Third. The least favorable temperature for its formation, within the annealing and *cold rolling* range, is below 600 degrees. The other extreme of temperature, 720° C., is also less favorable to its formation, but scaling goes on so fast as to give undesirable finish.

Fourth. The reason that black fracture is associated with cold rolling is that during this process the steel is worked and repeatedly reheated within the range of temperature where graphite forms rapidly. The steel has really had a series of anneals between 660 and 700° C.

Fifth. The longer the anneal is continued *at any annealing temperature*, the more graphite will be formed.

Prior to cold rolling, that is, when the steel gets its very first anneal for softening purposes only, hold it at 700 to 720° C. Keep it as near the highest annealing heat as possible, as by so doing a quick anneal is obtained without formation of graphite.

But when reheatings occur during cold rolling do this reheating at the lowest heat practicable, for around 580 to 600° C. graphite does not form as fast as at 660 to 700 degrees, nor does scale. *Let the periods of annealing and reheating be as short as possible.*

Sixth. By heating steel to 950 to 1000° C. for one or two hours, then turning down the gas so that the steel cools in the furnace to 660 to 700 degrees, and continuing to anneal at the latter temperature for a given length of time, graphite can be eventually formed in steel with carbon as low as 1.04 per cent. Therefore steel that is to be cold rolled should not be allowed to remain long in soaking pits or heating furnaces at high temperatures.

Steel containing chromium is not likely to contain graphite even with carbon as high as 1.27 per cent and chromium as low as 0.6 per cent. The writer succeeded in starting a graphitic formation in such a steel only by heating it to 900 to 1000° C., for an hour or two before annealing at 660 to 700° C. In neither this instance nor in the case of the 1.04 carbon plain steel did

there seem to be any appreciable tendency for a gradual growth of the graphite due to prolonged annealing only, even after the eleventh trial, making considerably over 100 hours' anneal. Perhaps if these samples had been again heated to 1000 degrees before each of the eleven anneals, an appreciable growth of graphite would have been noted. In neither instance was there enough graphite formed to be noticeable in the fracture.

To detect small amounts of graphite dissolve 0.100 gram of sample in a 152.4 mm. by 16 mm. tube (6 inches by 16 mm.) with 4 c.c. 1.20 nitric acid and heat on a water bath in boiling water for two hours in the case of chrome steel and one hour in plain carbon steel. Permit the solution to stand for several hours without agitation of the same to detect traces of graphite which can be plainly seen in this way in the bottom of the tube.

#### ACID TEST FOR ANNEALING.

\* Dissolve 0.100 gram of sample in 4 c.c. of cold 1.20 nitric acid. Examine immediately in daylight. If the undissolved carbon is flaky and floats about in the solution the steel is not annealed at all. It is in the condition in which it left the rolls or hammers. If on the other hand the carbon is in an extremely fine state of division, so much so that it does not separate in flakes at all, but rather tends to run up the sides of the test tube in a thin film, then the annealing is perfect and the steel has reached the highest degree of softness.

In perfectly annealed steel this finely divided annealed carbon will remain in almost complete suspension for some minutes. Indeed it cannot be seen to collect and settle as flakes, but settles imperceptibly, after some time, so that there exists a collection of fine powder, rather than flakes, in the bottom of the test tube. An ordinary 6 inch by 15 mm. carbon test tube † is best suited for these tests. Then, if it is desired to examine the

\* Reject surface drillings to the depth of at least  $\frac{1}{8}$ th of an inch when taking a sample for annealing test.

† Test tubes must be scrupulously clean, free from the slightest film of grease, or dirt, or other coating.

sample for graphitic carbon, the tube is put at once on a water bath in boiling water for one hour. By that time all of the combined carbon will have gone into solution and the graphite will be collected in a coal black residue in the bottom of the tube.

The operator soon learns to pronounce to an absolute certainty whether the steel is *perfectly* annealed or not. He also can judge whether much or little graphitic carbon is present.

This annealing test is carried out in ten minutes, and enables the chemist to pronounce unfailingly on the quality of the annealing before the steel is shipped to the customer. It gives a perfect control over the work that is being done by the man in charge of the annealing. A scale of annealing can be established. It has been the writer's custom to call perfect annealing, 5 degrees. Good enough for all practical purposes,  $4\frac{1}{2}$  degrees. Moderately good, 4 degrees. Partially annealed, 3 degrees, and so on. The quicker the carbon forms in flakes and separates, the poorer the annealing. As stated, good annealed carbon does not separate in flakes at all.

#### ANNEALING TEST WHEN ALLOYS ARE PRESENT.

When from 0.1 per cent to 1 per cent chromium is present in steel the annealing *carbide* is formed and acts differently from carbon in plain steel. It forms almost coal black; is not flaky; but the individual grains are coarser than in plain carbon steel.

A well annealed chrome carbide within the above chromium content forms in minute coal black grains that settle rapidly to the bottom of the test tube. The quicker the grains form, the blacker they are, and the more rapidly they settle to the bottom, the better the anneal.

This peculiarity constitutes an infallible test for the presence of chromium in steel, but the latter must be perfectly annealed to show as small a quantity as 0.1 per cent chromium in 0.100 gram of sample. More experience is required to pronounce on the annealing of chrome steel by the acid test, but with

practice one can be quite as accurate as when making the test on plain carbon steel.

In well annealed steel containing 3 per cent of chromium and over, the carbide is coal black but does not settle to the bottom nearly so fast as does the carbide found in perfectly annealed steel of 1 per cent chromium and under. The grains settle slowly, and there is a well defined film running up the walls of the test tube, but the grains should be in the finest state of division.

Plain tungsten steel, in the perfectly annealed state, gives practically the same appearance as ordinary carbon steel when tested for annealing.

Nickel and manganese steels act exactly as plain carbon steel when perfectly annealed. The color of the finely divided annealed carbon has perhaps more of a brown shade in high manganese and nickel steels, but it does not settle any faster than in plain carbon steels. One of the greatest difficulties in annealing steel is to obtain uniform heat throughout the entire furnace. The dividing line between a good annealing heat and hardening temperature is very sharp. The writer has had a piece of steel but two inches long exhibit perfect annealing on one end, while the other end had passed into the hardening range. He has also another piece that shows black fracture on one end, and the other end less than two inches away shows no trace of black fracture. These phenomena are due to unequal temperature in the furnace.

An annealing furnace should have several pyrometer couples located in different parts of it.

The pyrometers should be sent to the Bureau of Standards for occasional verification of their readings. They should not be used until their accuracy has been verified, as different instruments are liable to disagree as much as  $25^{\circ}\text{C}$ . from the Washington Standard.

## CHAPTER XVII.

### PART II.

- (1) FURTHER ANNEALING TEMPERATURES.
- (2) SURFACE DECARBONIZATION.

SUPPLEMENTING the annealing temperatures given on pages 340 and 341 one can calculate *approximately* the best annealing temperature for manganese and nickel steels by deducting from  $720^{\circ}$  C.,  $18\frac{1}{2}$  degrees for every per cent of manganese or nickel present; and on account of the similarity of cobalt to nickel the presumption is that the rule holds good for cobalt also. To determine *exactly* the best annealing temperature, one should first determine the critical point of the steel and then anneal it just under the critical point ( $Ar_2$ ). If one has no apparatus for critical point, then recourse can be had to the above calculation. The result can be checked by the acid annealing test given on pages 344 and 345 and the annealing trials continued until the chemical test shows the annealing is perfect.

#### ANNEALING TEMPERATURE FOR CHROME-MANGANESE STEEL AND CHROME-NICKEL STEEL.

In such steels there exists two independent annealing temperatures, that is the steel must be given an annealing as though it were chrome steel or about  $720^{\circ}$  C. and then the temperature should be lowered and the steel annealed as though it were a manganese steel, or a nickel, or cobalt steel, only.

Some of these manganese-chrome steels require as low as  $350$  to  $450^{\circ}$  C. to soften the manganese combination therein.

12 per cent nickel steel of low carbon (0.50% carbon) anneals well at about  $500^{\circ}$  C. Highly alloyed chrome-tungsten-vanadium steels with carbon over 1 per cent, alloyed further with 2 or 3 per cent of copper, must first be annealed for some hours at about  $850^{\circ}$  C. and then, curiously enough, must be given as low an

annealing as though 10 to 13 per cent of manganese were present. It is necessary to perform the annealing in this way before the steel can be drilled at all, even with the best Rex AA drill. The same kind of a steel with low carbon of about 0.60 per cent C does not require the low annealing temperature. This is a striking example of the fact that carbon has a marked influence on the annealing temperature in some cases. It no doubt has in all cases but the writer has never seen such marked effect in any other steels.

#### THE FORMATION OF "BARK" OR DECARBONIZED SURFACE ON PIPE-ANNEALED STEEL.

Several years ago, since the publication of the first edition of this book, the author investigated the cause of this troublesome soft surface and his conclusions were published in the following paper:

#### THE FORMATION OF WHITE SCALE ON STEEL AND THE SURFACE DECARBONIZATION OF PIPE-ANNEALED STEEL.\*

By CHARLES MORRIS JOHNSON.

*Received April 10, 1909.*

[Reprinted from the *Journal of Industrial and Engineering Chemistry*, Vol. I. No. 7. July, 1909.]

When bars of steel are annealed in pipes, with charcoal, to produce a scale-free, frosted, metallic finish, there is frequently found at the surface of the metal a coarsely crystalline structure *H*, *G*, Fig. 24, that is much lower in carbon content than the remainder of the bar. Such steel will not harden file-proof on the outside. It is rejected for that reason by makers of twist drills, though this defect be so slight as to require a magnifying glass for its detection.

In pipe-annealing the bars are put in a steel tube that is welded shut at one end. The spaces between the pieces are filled in with wood charcoal. The open end of the pipe is plugged

\* From a paper read at the March, 1909, meeting of the Pittsburgh Section of the American Chemical Society.

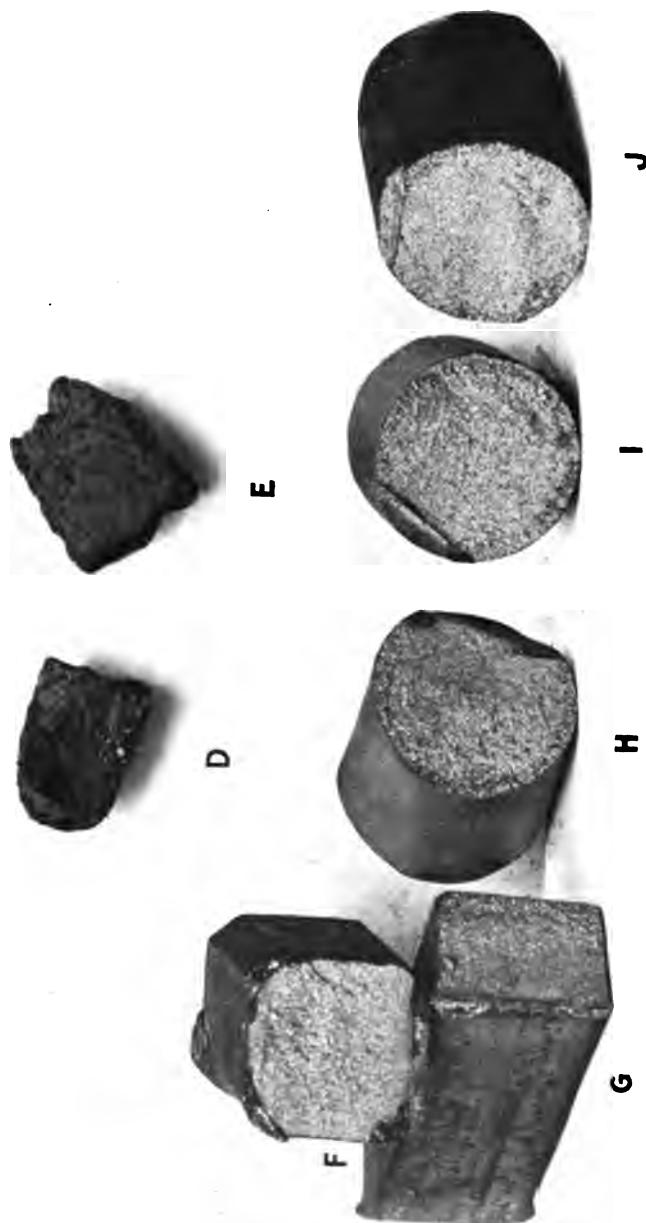


FIG. 24.

with fire brick, fire clay and a disc of plate steel. A small vent hole is located at one end of the pipe to permit the escape of the large quantity of carbon monoxide that is generated by the reaction between charcoal and the air yet remaining in the vessel. As apparently dry charcoal often holds considerable moisture in its pores, some water vapor must also be liberated.

The superficial decarbonization *G*, *H*, *I*, Fig. 24, is at times much more pronounced than at others. The writer became interested to investigate the process with a view to discovering the primary cause of this very objectionable feature of annealing in a closed tube.

In the first place it was soon noted that the condition frequently exists in steel before it reaches the annealer, due to forging at too high temperatures.

Again, it was deemed possible that the scale, always existing on the steel when it is put in the pipes, might react with the charcoal to form CO<sub>2</sub>. Further, that the latter gas would, under the existing conditions, decarbonize the steel by the reaction CO<sub>2</sub> + C = 2 CO.

To test this theory some  $\frac{5}{8}$  inch Rd., high carbon steel rods were placed in a porcelain tube and heated for 18 hours with a slow stream of pure, dry carbon dioxide passing through the enclosure. The following points were noted:

1st. A glittering black scale was produced on the fractured or otherwise unpolished surfaces of the bars. On fracturing the latter, a distinct ring of coarse crystals was found to exist at the margin of the fractures. This scale has a curious property of adhering in a thick, sparkling black mass on rough fractured surfaces, but when polished steel is exposed, at a red heat, to the attack of CO<sub>2</sub>, only a black discoloration resulted. The scale referred to, proved, on analysis, to be Fe<sub>3</sub>O<sub>4</sub>. This experiment showed that carbon dioxide may cause "bark" (surface decarbonization) but not to a marked enough extent to offer a satisfactory explanation.

2nd. Some pieces of the same bar were heated in a stream of pure, dry hydrogen. A frosted metallic surface was produced

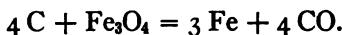
and also a slight "bark." Hydrogen, therefore, will decarbonize steel by forming hydrocarbons.

3rd. Next, a piece of the bar was heated in the closed porcelain tube, packed loosely with charcoal. First air was expelled, but, as the heat attained slight redness, large quantities of CO escaped at the outlet end. After an 18 hour heating, at about 750 to 780° C., a handsome frosted, metallic surface had displaced the black oxide and much decarbonization was noted. The carbon content of the bar before annealing was 1.08 per cent. The decarbonized zone yielded but 0.84 per cent.

4th. Thinking that CO gas might be the active agent in (3), a small clay boat was filled with about a tablespoonful of charcoal. The boat was then placed in the tube with a piece of the steel and the usual period of heating followed. The result was the same as in the third experiment. *Note.* Annealing in a stream of natural gas produced a sooty exterior and a heavy "bark" (see J, Fig. 24).

5th. The fourth trial suggested annealing a piece of steel in an EMPTY, CLOSED TUBE with NO CHARCOAL or other reducing substance! No attempt was made to remove the air except as it was partially driven out at the vent end by expansion. The only precaution taken was to prevent indrawing of more air, at *any time*, while the tube was *hot*. The same result was obtained as is shown in the white bars at C, Fig. 25, that is, an aluminum-like surface with great decarbonization underneath! This experiment was repeated with steel containing but 0.10 per cent carbon and also with steel containing large quantities of chromium and tungsten. The 0.10 carbon steel is given at B, Fig. 25.

The writer felt that he had now reached the first goal and that the most active agent in surface decarbonization is the rust or scale which is actually reduced to metal at the expense of the carbon in the steel to which it adheres:



In this connection the question arose, would steel with an extra heavy, loosely adhering scale perform in like manner? Or,

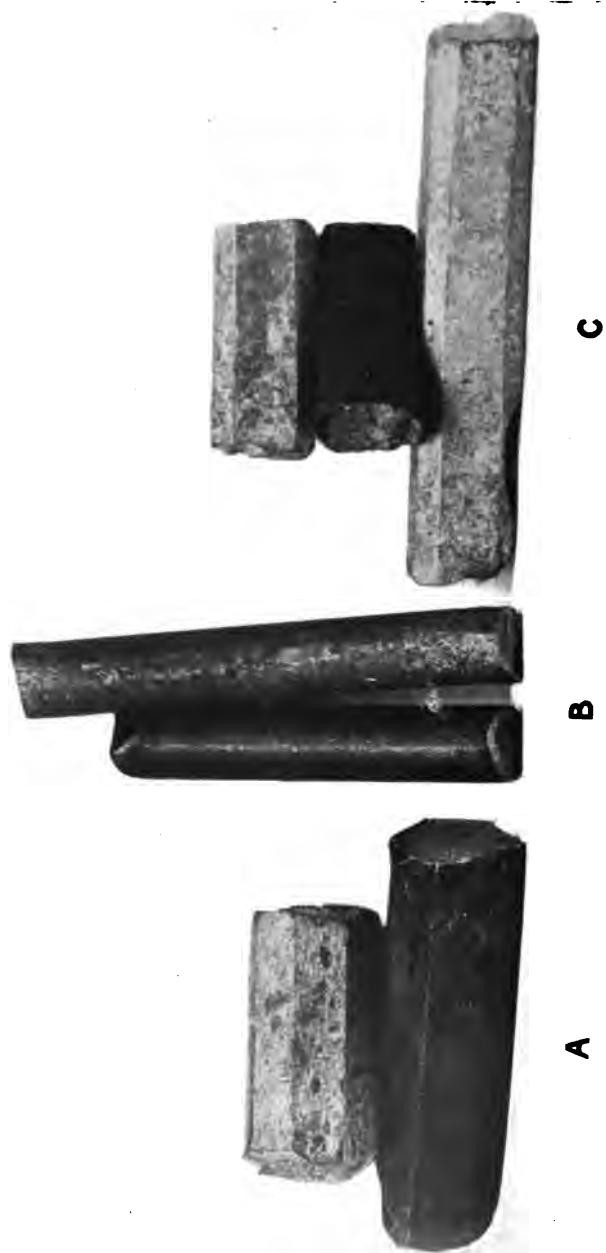


FIG. 25.

in other words, is close contact necessary for reduction? To settle this query a small piece of quarter octagon of saw analysis was given a prolonged heating in an *open* muffle at about 850° C. This treatment blistered the bar with a thick scale that was so loose that the sample had to be transferred to the annealing tube quite carefully to prevent the scale from being jarred off. After 15 hours' heating no change was noted, that is, the scale was still black. After a second heating of 18 hours the *surface* of the scale presented a slight *greyish* caste. After a third period of 18 hours' heating it was found that the heavy black scale was gone and, in its place, a *white*, loosely adhering, aluminum-like scale existed on the steel. Here, apparently, the black scale had begun to reduce on its top surface first.

This fact pointed to the existence of a reducing gas in the tube.

6th. The writer then placed a piece of high carbon steel in the tube, together with a porcelain boat containing some hard, semi-fused iron oxide obtained from a carbon combustion of steel drillings in oxygen. This hard, baked mass *D*, Fig. 24, was given 18 hours' heating at a temperature of about 850 to 900° C. The porcelain boat was removed and found to contain, instead of a dense baked mass, a loose, friable substance, and that the volume of it exceeded the original about  $2\frac{1}{2}$  times. The steel that had been in the tube was then fractured. It was exceedingly tough and disclosed a heavy surface decarbonization *G*, Fig. 24. The loose sponge of oxide was put back in the tube with a fresh piece of steel and given a second heating. This time the substance *E*, Fig. 24, in the boat had become light grey in color and was no longer friable but was now adherent and almost sticky in its clinging fibers. This material assayed 98 per cent metallic iron and, on being cut with a knife blade, presented a metallic luster. It occurs that here is a means of preparing pure metallic iron from pure oxide by heating it in a closed tube with a sealed vent (the writer used concentrated sulphuric acid for a seal), together with a piece of low sulphur, high carbon tool steel. Before turning off or lowering the heat

it is, of course, necessary to close all vents perfectly, otherwise air will be drawn in the tube and metallic iron surfaces will lose the aluminum-like luster and become blued. Metallic iron so prepared should certainly be free of occluded hydrogen, which constitutes an objection to electrolytic iron. Some specular iron ore was ground to a red powder and then reduced to a grey powder in this way.

A piece of steel *A*, Fig. 25, that had been lying in water for weeks and was covered with both black and yellow oxides was heated in an empty, sealed tube. The result was a white metallic surfaced sample. A piece of blue steel was heated four hours in an empty tube and the blue surface was replaced by a white aluminum-like one.

7th. Further experiments developed the fact that this scale forms much more rapidly at high temperatures, that is, those above 700 degrees. The higher the heat the more rapid the transformation from rust and black scale to the white and metallic scale. This white scale takes on the white appearance long before it is entirely reduced to metal. The author has had white scale that would be brittle and grind to a black powder. However, when the reduction is complete the scale is no longer brittle and cannot be powdered, but is entirely metallic in its properties.

8th. The corollary from the fact that white scale forms more slowly below 750° C. is that, at still lower ranges, perhaps below 650°, it may not form at all. Further experiments covering this point will be made.

9th. By annealing steel in a closed tube with a small vent to permit egress of gases but sealed against ingress of air, at temperatures close to 700° C., the surface decarbonization is so slight that no ring of coarser crystallization can be detected. Only a cupped effect can be noted around the margin of the fracture (see *F*, Fig. 24), yet such steel will take on a suggestion of the aluminum-like finish. Here the surface decarbonization is confined to the thinnest skin. Such steel hardens file-proof immediately under this extremely thin zone.

10th. By annealing steel that had been polished free of all rust and scale, in a tube from which ALL OXYGEN had been expelled by CO, no surface decarbonization was noted and the steel hardened file-proof. The CO was generated by heating wood charcoal.

11th. A rod of polished steel was dipped in a solution of copper sulphate until it was plated with metallic copper. After heating this rod in a closed tube, *without* expulsion of the air, for a few hours, the rod was removed from the tube and was found to be coated with a handsomely appearing metallic copper. During this experiment the tube was sealed against ingress of oxygen.

12th. By heating tungsten trioxide in a closed porcelain tube, and together with, but not in contact with, either a piece of steel or steel drillings, the writer was able to produce metallic tungsten powder of 99.98 per cent purity. The temperature required for this experiment was 1100° C. The tungsten oxide was in one porcelain boat and the steel drillings were in another.

## CHAPTER XVIII.

### PART I.

#### THE COMPLETE ANALYSIS OF LIMESTONE AND MAGNESITE.

(1) DISSOLVE 0.9 or 1.0 gram of the sample in 50 c.c. of 1 : 1 HCl in a No. 5 ( $4\frac{3}{4}$  inch) covered dish. Boil until all action is over, remove the cover and evaporate to dryness on the graphite bath; heat until the smell of acid is practically all gone. Cool; add 40 c.c. of 1 : 1 HCl; cover; boil with the lid on and evaporate to 20 c.c.; add 50 c.c. of water; boil with the cover on for a few minutes; add ashless paper pulp; filter; wash, first with dilute 1 : 40 HCl, and then with water until 20 drops of the washings do not give even a slight milkiness with silver nitrate solution. Smoke off the paper in a platinum crucible and then raise the heat to bright redness until all black is gone and the ash in the crucible is from a pure white to a grey, depending on the grade of the limestone. Weigh the ash after it has been cooled in the desiccator and calculate it as insoluble residue. Fuse this insoluble residue, which consists of silica contaminated with some lime, oxide of iron and magnesia, with 20 times its weight of anhydrous sodium carbonate; dissolve the residue out in water in a platinum dish with heat or in porcelain in the cold in HCl if no platinum dish is available; acidulate the water solution with an excess of HCl; heat with the lid on until all spraying due to the escape of carbon dioxide is over and evaporate to hard dryness, twice, filtering after each evaporation. Moisten the residue in the dish with 10 c.c. of conc. HCl; heat; add 50 c.c. of water; boil five minutes; add a little paper pulp; filter and wash as in the case of the insoluble residue; ignite until the ash is pure white and weigh as pure silica. As an extra precaution against the presence of sodium salt it is more accurate to volatilize silica as in steels with HF and a few drops of  $H_2SO_4$ , page 286.

(2) The filtrate from the pure silica is added to the main filtrate and washings obtained from the insoluble residue. These combined filtrates contain all of the calcium, magnesium, iron and aluminum. A slight excess of ammonia is added to the nearly boiling filtrates to precipitate the iron and aluminum. A little paper pulp is well stirred in; the hydroxides are filtered off; washed with water, redissolved, and precipitated as before to insure the complete separation of the calcium and magnesium. The reprecipitated iron, etc., is washed free of chlorides with water and ignited to a constant weight in a platinum crucible as  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and calculated as such to percentage.

The filtrates from the double precipitation of the iron are combined, evaporated to 600 c.c., heated to boiling, and the calcium is precipitated with 50 c.c. of a saturated solution of ammonium oxalate. This amount of oxalate is added not only to precipitate the calcium but to insure an excess of the oxalate in sufficient quantity to hold the magnesium in solution as the latter is soluble in an excess of the oxalate.

The oxalate of calcium should stand for at least several hours when it is filtered off, after mixing it with considerable paper pulp. Wash it with oxalate water (5 grams of ammonium oxalate dissolved in 500 c.c. of water) until the washings, acidulated with a few drops of nitric acid, fail to give a reaction with silver nitrate. The calcium oxalate, to insure against the co-precipitation of a portion of the magnesium, should be dissolved in HCl, the filter thoroughly washed and the calcium reprecipitated as before, this time adding 25 c.c. of the ammonium oxalate. The reprecipitated calcium oxalate is filtered, washed, ignited, and finally blasted to constant weight as calcium oxide, which weight multiplied by 1.7847 gives the equivalent weight of calcium carbonate which is calculated to percentage as such.

The filtrates and washings from the two precipitations of the calcium oxalate are combined and evaporated to about 200 c.c. in the case of limestone, or to about 400 c.c. if magnesite. The solution, which should contain no crystals, is made slightly ammoniacal and 20 c.c. of a saturated solution of microcosmic

salt are added if the sample is limestone; if it is magnesite, 50 c.c. of the latter salt are used. The volume is then increased one-third with strong ammonia. The solution and precipitate are given a prolonged stirring, especially if the precipitate is slow in forming. After twelve hours have elapsed the ammonium magnesium phosphate is filtered off and washed free of chlorides with a mixture of 80 c.c. of conc. ammonia, 400 c.c. of distilled water and 5 grams of ammonium nitrate. The washed precipitate is smoked off in a platinum crucible and then the heat is raised to bright redness. The residue in the crucible is stirred from time to time until it is finally pure white. It is then cooled in a desiccator and weighed as magnesium-pyrophosphate, which multiplied by 0.7572 gives the equivalent weight of magnesium carbonate.

The calcium oxide and the magnesium pyrophosphate, after having been ignited to a constant weight, should be dissolved in HCl and the milligram or two of silica that is almost invariably present should be filtered off, washed, weighed and deducted from the calcium oxide and the magnesium phosphate before the final calculations to carbonate are made.

The filtrates and washings both from the calcium oxalate and the ammonium magnesium phosphate should be tested in every instance with further additions of the precipitants to make sure that precipitations have been complete.

#### SOME ANALYSES OF LIMESTONE.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
	Percent	Percent	Percent	Percent	Percent	Percent
Calcium carbonate.....	94.20	93.21	94.71	98.80	81.35	90.30
Magnesium carbonate.....	1.51	1.44	2.02	0.26	3.08	1.86
Oxides of iron and aluminum.....	0.09	3.20	1.46	0.26	3.12	2.46
Silica or insoluble residue.....	4.16	1.80	1.46	0.31	11.68	5.26

Samples Nos. 2, 3 and 4 are good limestones for basic open hearth purposes, being low in silica and over 93 per cent in calcium carbonate. Nos. 1 and 6 are doubtful and No. 5 is distinctly bad.

## SOME ANALYSES OF MAGNESITE. (Burned.)

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
	Percent	Percent	Percent	Percent	Percent	Percent
Magnesium oxide (MgO).....	85.09	83.33	85.00	83.21	86.19	84.44
Calcium oxide (CaO).....	3.88	3.22	3.88	4.32	2.66	3.24
Silica (SiO <sub>2</sub> ).....	1.84	1.16	1.84	3.00	4.59	6.00
Oxides of iron and aluminum (Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> ).....	8.38	8.22	8.38	8.92	5.52	5.90
Ignition loss.....	.....	5.06	.....	.....	.....	.....

In determining the magnesia in burned magnesite lime and fire-brick multiply the weight of Mg<sub>2</sub>PtO<sub>7</sub> obtained by 0.36206 to obtain the equivalent in magnesia (MgO).

## FIRE-BRICK ANALYSES. (Silica Brick.)

	No. 1.	No. 2.
	Per cent	Per cent
Silica.....	96.12	95.99
Oxides of iron and aluminum.....	2.00	1.71
Calcium oxide.....	1.50	1.88

## THE VOLUMETRIC DETERMINATION OF CALCIUM.

The calcium oxalate obtained as given in the gravimetric method is washed free of chlorides with water alone. The oxalate is washed off the filter as far as possible with a fine jet of water into a beaker. The oxalate remaining in the filter paper is dissolved out with 40 to 50 c.c. of 1 : 3 sulphuric acid and this acid solution is allowed to run into the beaker containing the main oxalate of calcium. The filter is thoroughly washed with 1 : 20 H<sub>2</sub>SO<sub>4</sub>. The filtrate and washings are warmed until all of the calcium oxalate is dissolved. The solution is then diluted to 350 c.c. with water and heated nearly to boiling and titrated to a faint pink with N/10 KMnO<sub>4</sub>, 1 c.c. of which is equal to 0.0020035 gram of Ca.



By (1), 1 Ca equals 1 H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

By the equation on page 199,  $\frac{1}{2} \text{KMnO}_4 = 5 \text{H}_2\text{C}_2\text{O}_4$ , hence  $2 \text{KMnO}_4 = 5 \text{Ca}$ , or 316.06 parts by weight of KMnO<sub>4</sub> correspond to 200.35 parts of calcium, or 3.16 grams of KMnO<sub>4</sub>, N/10 dissolved in a liter volume will have a value of 1 c.c. equals 0.002 gram of calcium.

## CHAPTER XVIII.

### PART II.

#### THE ANALYSIS OF OPEN HEARTH BOTTOM SAND AND FIRE-BRICK.

THE sample is ground to the fineness of flour in an agate mortar. It is then dried for one hour at a temperature of 105 to 110° C. While the dried sample is still warm, it is put into a clean, dry glass stoppered bottle where it is cooled before using. 1 gram and, for a check, 0.9 gram are taken for the analysis, being weighed into 30 c.c. platinum crucibles together with 10 grams of anhydrous sodium carbonate. This flux is well mixed with the sample by stirring it with a wire. The thorough mixture of sample and carbonate is heated gradually to redness and kept at a bright red heat until the mass in the crucible, which should be in a molten state, is in quiet fusion, that is with no bubbles of CO<sub>2</sub> escaping.

The melt is then cooled, and the crucible and contents are placed in a platinum dish, containing about 100 c.c. of water which is kept just below boiling until the fusion is dissolved, leaving only a stain in the crucible and a floating mass in the dish which should be free from grit. The dissolved fusion is then transferred to a 600 c.c. casserole and acidulated with 50 c.c. of conc. HCl, keeping the casserole covered with a watch glass during the very gradual addition of the acid. (In case a platinum dish is not at hand, dissolve the fusion in a casserole, in an excess of 1 : 1 HCl.)

The crucible in which the fusion was made is warmed with 5 c.c. of 1 : 1 HCl in it, to dissolve the traces of iron that still adhere to its inner walls. These cleanings are added to the main part in the casserole which is now warmed with the cover on until the carbon dioxide is mainly expelled. The watch glass

cover of the casserole is rinsed off and evaporation to dryness follows. To render the silicic acid insoluble, the dry residue in the casserole is given a further heating at a temperature of about  $120^{\circ}$  C. for an hour. Care should be taken not to exceed this temperature to avoid the possibility of loss of iron by volatilization of its chloride.

The thoroughly baked residue is cooled; moistened with conc. HCl, using about 20 c.c. of the acid, to dissolve the oxides of iron and aluminum; heated with the cover on to insure complete solution of the oxides; warmed with 200 c.c. of distilled water for a half hour with frequent stirring to secure as nearly as possible a perfect extraction of the large quantity of sodium chloride formed. Ashless filter pulp is added to the extraction, after it has been cooled, and stirred in with the now insoluble silicic acid. The mixture of pulp and silicic acid is poured on a double 15 cm. filter, that is, on to a filter consisting of two papers folded together. Such a filter will invariably secure more rapid and perfect filtration in the long run than a single filter.

The pulp and precipitate are washed, alternately, with water and 1 : 20 HCl until the washings are free from iron test, no longer giving a reddish tint with potassium sulphocyanate solution. Then the washing is continued with cold water until a few drops of the washings no longer give a white turbidity with a water solution of silver nitrate. The filters and pulp are then removed to an air bath and dried at  $120^{\circ}$  C. until most of the water is gone. The filtrate and washings are evaporated to dryness, warmed with acid, leached with water, filtered, washed free of iron and chlorides, as before, to obtain that part of the silicic acid that may have escaped complete dehydration in the first evaporation.

The filtrate and washings from this second filtration are retained for the main part of the iron, aluminum, calcium and magnesium. This filtrate and washings for reference are designated as A. The residues on the filters from the first and second evaporation, after having been freed from the excessive amount

of wash water retained by the pulp, by drying in the air bath, are placed in as large a platinum crucible as is available and the volatile matter in the paper is smoked off, cautiously. The crucible is then brought slowly to redness and the heating is continued until the ash in the crucible is pure white. The blast is applied for ten minutes, the crucible is cooled in the air for a moment, and placed in a desiccator until entirely cold, when it is weighed. The crucible is blasted again, cooled and weighed until a weight is obtained that does not differ from the last weight more than 0.0002 gram. This weight is taken as the final weight of the total silica together with a few milligrams of the Ca, Mg, Fe, Al, Ti, and a little of the sodium salts that cannot be entirely washed out. The true silica is then gotten by the loss of weight by volatilization with about 20 c.c. of hydrofluoric acid and 10 drops of conc. sulphuric acid, as in steels. The HFl is added a little at a time to prevent loss by too violent escape of the silicon fluoride. The evaporation is carried on in a good draft until thick fumes of the sulphuric anhydride appear. It is advisable to evaporate off the HFl in a specially prepared place to prevent the etching of the hood windows. Such an arrangement can be built in a wide chimney in the form of an arched space. The writer places therein a large agateware pan filled with a layer of graphite. To provide a clean spot on which to stand each crucible a number of nickel disks or lids of nickel crucibles are arranged on top of the graphite. The pan is heated with a Bunsen burner. About two feet above the pan, supported by offsets in the brickwork, is an asbestos board  $\frac{1}{4}$  inch thick which entirely prevents any foreign matter from falling into the open crucibles during the evaporation. A still better plan is to construct a small reverberatory furnace, lining it with asbestos board, heating it from above by a flame behind a bridge wall. Of course such a furnace is never allowed to get above a drying heat for these evaporation. Fig. 26 shows the construction of such a furnace, which with natural gas and compressed air can be brought to  $1300^{\circ}$  C., or can be kept at a mere desiccating heat by burning a small yellow flame in the combustion chamber C.

When the fumes of sulphuric anhydride no longer appear, the crucible is removed from the drying chamber and heated to

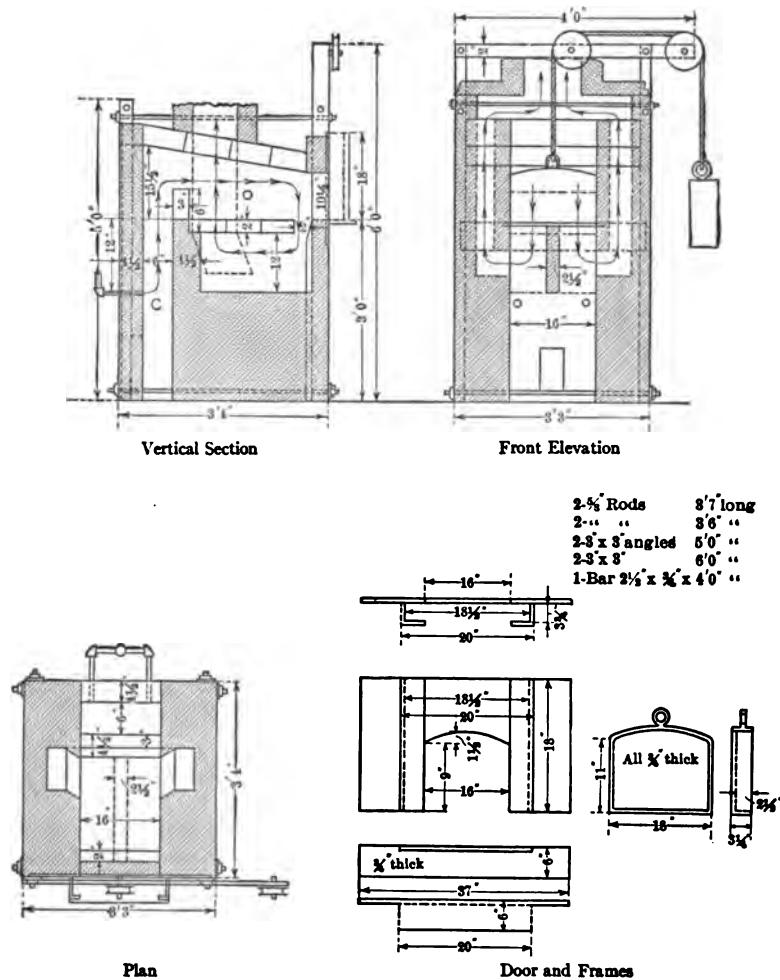


FIG. 26.

low redness only, in order to drive off any remaining sulphuric acid, and yet not hot enough to volatilize any sodium salts that may have contaminated the silica and remained behind after the

latter was evaporated away as fluoride. The crucible is then cooled in the usual way by placing it, while it is still warm, in a desiccator and then weighing it when cold. This weight is deducted from the previous weight of the crucible and its contents obtained by blasting to a constant weight. The difference so obtained is calculated to percentage as silica.

If the analyst wishes to be entirely certain that all of the silica has been completely removed, he should repeat the evaporation with HFl, using but 10 c.c. of the acid and also 10 drops of the H<sub>2</sub>SO<sub>4</sub>. If the crucible does not lose any weight on the second evaporation and ignition then the operator has proved the work. As previously stated, the residue in the crucible, after these evaporation, may contain traces of all of the elements present in the sand except silica. Therefore, the residue is fused with 20 times its weight of the sodium carbonate and is dissolved out as in the original main sodium carbonate fusion of the sample, and the acidulated fusion and the cleanings of the crucible are added to filtrate A which will now contain the total Ca, Mg, Al, Fe and Ti in the sand or brick.

Filtrate A is now evaporated to 350 c.c., heated to nearly boiling and filtered; 1 : 1 ammonia is added to it until it smells slightly but distinctly of ammonia. Much excess of ammonia will prevent a part of the aluminum hydroxide from precipitating. To avoid the tedium of long boiling, add the slightest possible excess of ammonia. If the solution smells strongly of ammonia, then the excess of the latter should be neutralized with some HCl. Having the conditions of alkalinity just right, the solution is boiled for five minutes, the beaker is removed from the fire and some paper pulp is stirred in, in large or small quantity according as the precipitate seems large or small. The precipitate, which will contain all of the Fe, Al, Ti and P in the sample, is filtered off on a double filter and washed with a solution consisting of 5 grams of ammonium nitrate dissolved in 500 c.c. of water. This is continued until the washings do not give the test for chlorides with silver nitrate. The precipitate is dissolved off the filter with hot HCl and reprecipitated

as before with ammonia; filtered, and washed. The second precipitate is burned off and blasted to a constant weight as in the case of the silica. The weight obtained is recorded as  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ .

The combined oxides are then dissolved by prolonged heating with conc. HCl, and if any white, floating residue remains insoluble it is filtered out; washed thoroughly in the same way as the main silicic acid, weighed, deducted from the total weight of the iron oxide, etc., and added to the total silica. The filtrate from this milligram or two of silica is reduced with stannous chloride and the iron titrated with the dilute potassium dichromate, page 186, to obtain the amount of iron present. The latter is then calculated to ferrous oxide,  $\text{FeO}$ . It is also calculated to  $\text{Fe}_2\text{O}_3$  and deducted from the total oxides of iron, alumina, etc. The remainder is calculated to percentage as oxides of Al, etc. ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , etc.).

The filtrates and washings from the two precipitations of the iron and aluminum are analyzed for lime and magnesia exactly as directed for limestone, beginning at the point where the combined filtrates from the double precipitations of the iron are combined, heated to boiling, and the calcium is precipitated with a saturated solution of ammonium oxalate, the only difference being that the lime content is only a per cent or two so that but 25 c.c. of the ammonium oxalate are used to precipitate the calcium present.

The ignition loss is obtained by blasting 1 gram of the sample to a constant weight. The first weight is taken after 10 minutes' blasting. The sample is then blasted for five-minute intervals, until it either no longer loses more than 0.0002 gram or begins to gain weight.

When analyzing sand or brick, blanks should be run including the fusing of 20 grams of the carbonate of sodium and the putting of the solution of this melt through every operation. The iron, silica, etc., so found should be deducted from that found in the sample. There is almost certain to be some iron and silica obtained from the chemicals and glassware.

Some Analyses of Sands.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	Percent	Percent	Percent	Percent	Percent
Ignition loss.....	0.40	0.47	1.20	0.64	.....
Silica.....	98.08	95.86	94.00	96.86	95.86
Oxides of iron, aluminum, etc.....	1.37	2.84	4.4	2.22	4.86
Calcium oxide.....	.....	.....	0.15	0.38	.....

Sand No. 1 is not suitable for open hearth bottoms as it does not bond well with the bottom but floats into the slag and, as a result, the steel bath cuts through the bottom in places. No. 3 is a good sand as it contains just about the right amount of oxides of iron, etc., to bond well. No. 5 should also be a good bottom sand.

#### TITANIUM.

Titanium is a frequent constituent of fire brick. The best way to determine this element is to obtain the *total* iron and aluminum from a separate one-gram portion. The hydrochloric solution of this iron, etc., is then fumed with 60 c.c. of 1 : 3 sulphuric acid and this residue is then analyzed as given for titanium either by color or gravimetrically as in steels.

## CHAPTER XVIII.

### PART III.

#### THE ANALYSIS OF IRON ORE.

*Metallic Iron.* Dissolve 0.400 and 0.500 gram of the floured sample (dried at 105° C.) with mild heating in 40 c.c. of conc. HCl until the insoluble residue is white and floating and free from any dark colored grit. When the insoluble portion shows no further change, the total sample is transferred to a porcelain dish and evaporated to dryness, in case the insoluble part is not pure white. This evaporation must be done under mild heat to insure against volatilization of iron chloride. Redissolve with 20 c.c. of conc. HCl, using heat and keeping the dish covered. Add 50 c.c. of water, stir in a little ashless paper pulp filter, wash with dilute HCl until the washings are free of iron test with KCNS. The filtrate and washings will contain all of the iron if the residue was pure white before the evaporation; but if it is the least bit colored there is possibility of it retaining some of the iron. It is at all times advisable, for close work, to burn the paper off until all black due to carbon is gone and then fuse the ash with twenty times its weight of sodium carbonate at a bright red heat for a half hour. This renders all of the iron, in the shape of silicate or titanate, soluble in HCl. The fusion is then dissolved out with a little water, an excess of HCl is added, and the solution is evaporated again to dryness, redissolved, filtered and washed exactly as described for the original main sample. This filtrate and washings will contain all of the iron, if any, that remained in the original insoluble portion; it is added to the first main filtrate and washings obtained after the first evaporation to dryness. These combined filtrates and washings are concentrated to 200 c.c. and heated to nearly boiling in a beaker. Stannous chloride is added a drop at a time, with stirring, until the hot

solution is water white, and then not more than 2 or 3 drops in excess. Place the 600 c.c. beakers in cold water until room temperature is attained. Then as each test is about to be titrated, add to it 40 c.c. of mercuric chloride solution and stir well. This should produce a silky white precipitate of mercurous chloride, taking care of the excess of the tin chloride. It is undesirable to have a large excess of the tin chloride as there is danger of producing a grey precipitate of metallic mercury which renders the titration inaccurate; and again a huge precipitate of mercurous chloride is undesirable.

The solution being properly reduced, it is titrated with a standard solution of recrystallized potassium dichromate, until two or three drops of the solution of the ore no longer give a blue spot test with the ferricyanide indicator but an orange color, instead.

#### REDUCTION BY METALLIC ZINC AND TITRATION WITH POTASSIUM PERMANGANATE.

After getting the ore in perfect solution by any of the foregoing means, the solution is converted to sulphates by evaporation to thick white fumes with 80 c.c. of 1 : 1  $H_2SO_4$ . The iron sulphate is then dissolved again by heating to boiling for some time with 100 c.c. of water. The solution is transferred to an 800 c.c. cone flask and diluted to 200 c.c. A stream of  $CO_2$  is passed through the flask. A total of 40 grams of zinc are added in portions to reduce the ferric iron. Heat, when the action of the zinc becomes slow, and continue to pass the  $CO_2$  until the zinc is all dissolved. Cool to room temperature with the  $CO_2$  passing. The  $CO_2$  is purified by passing through two wash bottles as illustrated on page 295, photo No. 21.

A blank of the same amounts of sulphuric acid and zinc should be run. In a blank the solution, toward the last, is very slow, and when there remains only about 0.5 gram of zinc, undissolved, the heat can be shut off and the solution cooled; a stopper is placed rather loosely in the flask and the latter is then let stand at room temperature until the next day, when the zinc will have completely dissolved and the blank can be titrated and deducted.

The iron can be reduced with aluminum as described for uranium on page 296.

In these titrations the end point is taken as the first pink color that spreads entirely through the solution and lasts but a few seconds.

The permanganate can be standardized by putting a similar weight of the "Sibley" iron ore standard through all of the operations, or with sodium oxalate, or with oxalic acid, as given on page 49.

(1) It would seem convenient, at this point, to give the reactions involved in the method.

(2) *The reaction between the ferrous iron and the dichromate* proceeds as follows:  $K_2Cr_2O_7 + 6 FeCl_2 + 14 HCl = 2 KCl + 2 CrCl_3 + 6 FeCl_3 + 7 H_2O$ .

(3) The following equation explains the reduction of the ferric chloride by the stannous chloride:  $SnCl_2 + 2 FeCl_3 = 2 FeCl_2 + SnCl_4$ .

(4) The excess of the stannous chloride is prevented from interfering with (2) by the mercuric chloride reacting to form mercurous chloride:  $SnCl_2 + 2 HgCl_2 = Hg_2Cl_2 + SnCl_4$ .

(5) If too great an excess of the stannous chloride is present, a grey precipitate of metallic mercury is produced which renders the titration inaccurate and the analysis must be repeated on a new portion:  $Hg_2Cl_2 + SnCl_2 = SnCl_4 + 2 Hg$ .

#### STANDARD AND SOLUTIONS.

*The dichromate* is made by dissolving 4.9 grams of the recrystallized salt in water and diluting to one liter.

*The stannous chloride* is made by dissolving 12.5 grams of granulated tin in 125 c.c. of conc. HCl or 20 grams of the stannous salt in 100 c.c. of the conc. HCl.

*The mercuric chloride* consists of 50 grams of the salt dissolved in one liter of water.

*The ferricyanide* for the spot test has a concentration of 0.5 gram per 100 c.c. of water and should be made as used.

## STANDARDIZATION.

The standardization is best effected by putting 0.3 and 0.4 gram of the U. S. standard "Sibley" iron ore, or some other ore that has been standardized with equal care (this latter standard is very convenient in that it is entirely soluble in HCl), through all of the foregoing operations and noting how many cubic centimeters of the dichromate standard are required to oxidize the known amounts of the iron standard. By so doing, an average value, for example, of 1 c.c. of the standard equals 0.00546 gram of metallic iron was obtained.

*Manganese.* Dissolve 0.100 and 0.050 gram of the powdered ore in 25 c.c. of conc. HCl. For close work filter out any insoluble matter, wash it and fuse as described under the determination of metallic iron. Dissolve out the fusion; acidulate it with HCl and add this now completely decomposed residue to the main solution; add to the latter 20 c.c. of 1 : 1  $H_2SO_4$  and evaporate to thick fumes; cool; add 20 c.c. of conc. nitric acid and 20 c.c. of water and heat until all of the iron and manganese sulphates are dissolved and nothing remains but the floating silicic acid. Then transfer from the porcelain dish to a cone flask, or a 10 X 1 inch test tube, rinsing with 1.20 nitric acid, and finish as in steels. (See page 276.)

If the manganese exceeds 2 per cent, 1.0 and 0.9 gram are gotten into solution as above and the analysis can be finished by the phosphate method or by the ferricyanide titration, page 188 or page 193.

*Phosphorus and Silica.* Dissolve 0.9 and 1.00 gram, as for the metallic iron, using 40 c.c. of conc. HCl, fusing the insoluble residue and placing the acidulated melt back in the main solution; then evaporate to dryness; adding 1 gram of chlorate of potassium before evaporating, heating with the cover on the porcelain dish until all action caused by the addition of the chlorate is over. After the evaporation to dryness, redissolve in 20 c.c. of conc. HCl; evaporate to 10 c.c.; add 20 c.c. of water; add a little ashless filter pulp; filter and wash with 1 : 40 HCl until

the washings no longer give an iron test with KCNS; evaporate the filtrate and washings again to dryness on the graphite, dissolve, dilute, filter and wash as before to insure the separation of all of the silica. The filters from the first and second evaporation to dryness contain the total silica and are ignited and finished for silica as in steel (page 286).

The filtrate from the second filtration and washing contains all of the phosphorus; it is evaporated low and is converted to nitrates, boiled with permanganate, and finished for phosphorus as in steel (page 258).

*Sulphur.* Fuse 1.0 and 0.9 gram, as given for ferro-vanadium at the bottom of page 17, running blanks as a check on the reagents.

*Aluminum, Calcium and Magnesium.* Get 0.9 or 1.0 gram into solution and evaporated to dryness as for silica. The filtrate from the second evaporation will contain all of the aluminum, iron, manganese, most of the titanium, all of the phosphorus, calcium and magnesium. Make a double basic acetate precipitation of the filtrate as described on pages 188 and 189 and combine the two sets of filtrates and washings for the calcium and magnesium. The precipitate from the second basic acetate precipitation is burned off at a low heat, blasted to constant weight, and weighed as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ . The residue in the crucible is then dissolved in conc. HCl and divided into two parts; the phosphorus is determined in the one part after converting it into nitrate as described under phosphorus; and in the other part the metallic iron is found as given under metallic iron, by reducing this half with stannous chloride. The iron so found is calculated to  $\text{Fe}_2\text{O}_3$ , multiplied by two and deducted from the total weight of the oxides. In the same way the phosphorus found is calculated to  $\text{P}_2\text{O}_5$ , multiplied by two and deducted. This leaves only the weight of the  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . The latter is determined on a separate portion and calculated to a one-gram basis and deducted, leaving the aluminum only.

Also these same weights of ore can be gotten into solution

as for silica, the silica filtered off; the filtrate and washings therefrom can be transferred to a 1 liter boiling flask and the iron, manganese and titanium can be removed by two or three peroxidations. The filtrates and washings from peroxidations can then be made acid and the aluminum precipitated at once with ammonia; redissolved and reprecipitated to remove the sodium salts that are inevitably present in the aluminum hydroxide. The reprecipitated aluminum hydroxide is weighed as  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ . The phosphoric anhydride is determined by fusing the two oxides in 20 times their weight of anhydrous sodium carbonate; the melt is dissolved in nitric acid and is then evaporated to 40 c.c. and finished as in steels, page 258.

This latter scheme is decidedly to be preferred if calcium and magnesium are not needed.

*Calcium and Magnesium.* The filtrates from the two basic acetate precipitations are combined and evaporated nearly to crystallization with 100 c.c. of conc. HCl. Then 200 c.c. of water, or more, are added and heat is applied until the salts are all dissolved. If any dirt or dust has crept into the solution the same is filtered out and the filtrate and washings are finished for Ca and Mg as in limestone from the point where the filtrates from the iron have been obtained and are ready for the addition of the oxalate. (See page 357.)

Also, if it is desired to obtain the latter elements in a separate portion one can proceed exactly as given for limestone (page 356).

*Titanium.* Fuse 1 gram with 20 grams of acid potassium sulphate and finish for titanium as directed on page 51, if the titanium content of the ore amounts to more than one per cent. If the per cent of titanium is less than one per cent, fuse as above but boil the sulphuric acid solution of the fusion obtained as directed on page 54 with some strong nitric acid and compare it with an iron ore, containing a known amount of titanium, that has been put through all of the operations. Dilute the sulphuric acid solution of the fusion to 100 c.c.; boil it five minutes with 25 c.c. of conc. nitric; cool and compare as given for steels on page 54.

*Copper and Nickel.* Dissolve the ore as far as possible with HCl, using 20 c.c. of the conc. acid per gram, heating a little below boiling in an 800 c.c. beaker until the insoluble residue does not show any further change, that is, does not grow any whiter. Use 15 grams of the finely ground sample if the copper and nickel do not exceed one per cent. When the HCl is apparently having no further effect, then add cautiously 10 c.c. of conc. nitric per gram of ore taken and also a total of 10 c.c. of hydrofluoric acid and digest the contents of the beaker for at least one hour.

Evaporate to moist dryness, but do not bake for fear of rendering the nickel insoluble; redissolve in 100 c.c. of HCl and evaporate until the solution does not seem to have a great excess of HCl; convert the solution to nitrate by evaporating until further additions of conc. nitric acid no longer produce red fumes or until a few drops of the solution give but little if any milkiness with silver nitrate solution. Then finish for copper and nickel as given on pages 149 to 152. Run as a standard an iron ore containing a known amount of copper, or if such a standard is not at hand, then add to the ore a known amount of copper and nickel and also run the same ore without any copper and nickel, performing the standardization in the same way as given for pig iron on pages 149 and 151.

*Chromium.* Determine the chromium exactly as given for chrome ore on pages 140 and 141.

*Ignition Loss, Carbon Dioxide and Moisture.* The ignition loss is obtained by heating 1 gram of the sample at a bright red heat for an hour.

Carbon dioxide and organic matter can be determined together as CO<sub>2</sub> by burning 1 gram of the sample in the electric combustion furnace for one hour in a stream of oxygen as in steels. The CO<sub>2</sub> existing as such can be determined by heating the ore with conc. HCl. in a flask through which a constant stream of air purified from CO<sub>2</sub> in the same manner as the oxygen is purified for the determination of carbon in steel, is drawn. The flask should be provided with a No. 6 rubber stopper. The

flask shown for sulphur work on pages 104 and 269 will answer. The stopper should be pierced with a funnel tube as shown on page 104; also an inlet tube for the purified air which should extend  $\frac{1}{4}$  inch below the acid in the flask; the stopper must also have an outlet tube extending through the stopper into the flask, but not touching the fluid in the same. This tube will conduct away the  $\text{CO}_2$  liberated by the digestion with HCl by means of gentle suction with a water pump connected to the outlet of the weighing apparatus. The weighing apparatus and the train between it and the outlet of the digesting flask can be made exactly as the same part of the carbon combustion apparatus. The whole apparatus can be thought of as parallel to the carbon outfit with the flask taking the place of the electric furnace. If it is more convenient oxygen can be forced through the apparatus, during the digesting period, instead of drawing air through the outfit. The weighing apparatus *J*, page 224, should be weighed after air or oxygen has been drawn through it during an hour's digestion. *J* is again attached and air passed through it for another half hour, but during this second passage of the air, or oxygen, no heating should be necessary. If there is no more gain of weight than a blank gives at this point, then it is proven that all of the  $\text{CO}_2$  has been drawn over into the weighing apparatus. The operator can check his apparatus and the accuracy of his manipulations by determining the  $\text{CO}_2$  in limestone containing a known amount of calcium carbonate or by taking a known weight of calcite crystals.

*The Moisture* is determined by weighing 1 gram of the sample and drying it to a constant weight at  $105^\circ\text{C}$ .

*Combined water* is determined as in an unburned crucible, page 330, using 1 gram of the sample that has been already dried for one hour at  $105^\circ\text{C}$ . and kept in a glass-stoppered bottle after the drying.

*Vanadium* is determined in the same manner as given for carnotite ore, page 301.

## CHAPTER XVIII.

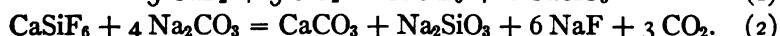
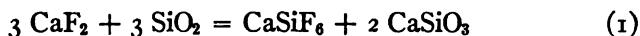
### PART IV.

#### THE ANALYSIS OF FLUORSPAR.

##### EXACT METHOD.

As this mineral is not completely decomposed by fusion with sodium carbonate alone, it is the general practice to fuse the finely ground mineral with a mixture of sodium and potassium carbonates, and finely ground precipitated silica. The author uses, for the melt, an intimate mixture of 1 gram of the sample with 10 grams of each of the two carbonates mentioned, together with 3 grams of precipitated silica.

The 1 gram of the spar is stirred carefully through the flux in a thirty-gram platinum crucible and the whole is gradually brought to a bright red heat and held at this temperature until all bubbling due to the evolution of  $\text{CO}_2$  ceases, indicating that the reactions are complete as follows:



When the fusion is finished in the manner indicated, it is run around the sides of the crucible; and, when cooled, the crucible is placed in a platinum dish and its contents dissolved in water with heat. If no platinum dish is available, then the melt *must* be dissolved in the cold in a porcelain dish. When all is dissolved except the floating portion, cool, add paper pulp, filter into a large casserole and wash the residue on the filter with 2 grams of sodium carbonate dissolved in 500 c.c. of water, giving the filter at least 50 washings, obtaining residue *R* on the filter, and the filtrate and washings *A*, which latter will contain all, or nearly all, of the fluorine as NaF and much silicic acid as sodium silicate, according to (2).

The main silica in filtrate *A* is separated according to the method of Berzelius, by heating with ammonium carbonate and removing the last traces with an ammoniacal solution of zinc oxide as follows: 20 grams of ammonium carbonate, in powdered form, are added to *A* and the same is heated for an hour at 40° C. *A* is then filtered after 12 hours. Considerable ashless filter pulp is stirred in with the precipitated silicic acid. The mixture of pulp, silicic acid and perhaps some iron and aluminum hydroxides is filtered out and washed with one gram of ammonium carbonate dissolved in 500 c.c. of water, at least fifty times, allowing each washing to drain off completely before the next one is applied. This filtrate and washings can be designated as *B* and contain the major part of the sodium fluoride and still some of silicic acid. The mixture of pulp and silicic acid on the filter from *A* can be marked *M*.

The residues *R* and *M* are smoked off in a large platinum crucible and then the heat is raised until the ash is free of charcoal and of a light brown color. In this way nearly all of the original added silica is returned to aid in attacking any undecomposed spar that may have escaped decomposition in the original fusion. Place on top of the ash from *R* plus *M* a ground mixture of 10 grams, each, of the carbonates of sodium and potassium. Stir this flux all through the ash *R* plus *M* with a stout Ni-Chrome wire and then repeat the fusion as described in the first place, and all of the other foregoing operations. The water-insoluble residue *R'* from the second fusion is washed with sodium carbonate water as in the case of *R*. This water-insoluble residue *R'* contains all of the calcium, barium, magnesium, iron and some of the aluminum. The filtrate and washings from *R'* contain any remainder of the fluorine and nearly all of the silicic acid and aluminum (if Al be present). This filtrate and washings are heated with ammonium carbonate as in *A*, allowed to stand for some hours, filtered, washed with ammonium carbonate water, obtaining a residue *M'* on the filter consisting of nearly all of the silicic acid plus a little iron and aluminum. The filtrate and washings from

*M'*, i.e. *B'*, contain the last traces of the silica. This filtrate combined with *B* contains all of the fluorine as sodium fluoride and the remainder of the silica as sodium silicate. This silica is removed as follows: Evaporate these filtrates to dryness in a casserole; take up with as little water as possible; add a few drops of an alcoholic solution of phenolphthaleine and then add 1 : 1 HCl until a few drops of this acid just discharge all pink color. The solution is then boiled to note if the pink color may reappear, and if it should, a drop or two more of the acid is added to just remove the pink and so on until no pink reappears on heating. The solution will then be neutral and is ready for the removal of the last traces of the silicic acid by means of a saturated solution of zinc oxide in ammonia, prepared as follows: Dissolve 10 grams of zinc oxide in 50 c.c. of conc. ammonia and filter off the undissolved zinc oxide. Add 10 or .12 c.c. of this filtrate to the neutralized *B* plus *B'* to precipitate the silicious matter still remaining therein, as zinc silicate. After adding the ammoniacal zinc solution, boil until the smell of ammonia is gone, and then filter out the mixture of zinc silicate and zinc oxide and wash it with 5 c.c. of the ammoniacal solution of zinc oxide diluted with 500 c.c. of water, obtaining filtrate and washings *C* which contain all of the fluorine as sodium fluoride and free of silica. The silicic acid gotten from *B* plus *B'* as zinc silicate is freed from zinc by dissolving it off the filter with nitric acid, 1.20, and evaporating the filtrate and washings so obtained to dryness. The dry residue is taken up with 1.20 nitric acid and filtered off, after dilution with water, on the same filter from which the zinc silicate was dissolved with nitric acid. The residue on this filter is washed thoroughly and burned off with *M'*.

*The Calcium Fluoride.* The filtrate *C* is heated to boiling and the fluorine is precipitated from it while boiling by means of a saturated solution of calcium carbonate. Some recommend the addition of a little sodium carbonate before adding the precipitant, thus causing a precipitation of some calcium carbonate along with the calcium fluoride to aid in the subsequent filtration.

The calcium fluoride is filtered and washed thoroughly with water. It has been the writer's experience that it requires not less than 50 washings to completely wash a large precipitate. The  $\text{CaF}_2$  is burnt off in a platinum crucible at a very low heat, just smoking off the paper, and then at low red to remove the carbon.

The ash which consists of a mixture of oxide, fluoride and carbonate of calcium is dissolved with dilute acetic acid (three parts of the acetic acid diluted with 1 part of water), by heating and evaporation to dryness on the water bath. The calcium fluoride remains insoluble and the calcium carbonate and oxide are dissolved. After the evaporation to dryness, 50 c.c. of water are added to the dry residue and heat is applied for about a half hour. The insoluble calcium fluoride is filtered off and washed with water, dried, ignited at a low heat and finally at redness until the  $\text{CaF}_2$  is white, when it is cooled and weighed and calculated to percentage as such. As a check on the purity of the  $\text{CaF}_2$  it is evaporated to dryness with 5 c.c. of conc.  $\text{H}_2\text{SO}_4$ . The excess of sulphuric acid is driven off at a low red heat and the residue is weighed as calcium sulphate, 1.7438 grams of which equal 1 gram of calcium fluoride.

*Silica.* The water-insoluble residue  $R'$  is smoked off in a platinum crucible and then heated at redness until all carbon from the paper is gone. The ash which contains the main calcium, etc., is transferred to a porcelain dish and boiled for a few minutes with 30 c.c. of 1 : 1 HCl until all but perhaps a little silica is dissolved. The latter is filtered off, washed, designated as  $M''$  and burned with  $M'$ . The ash from the burning of  $M'$  plus  $M''$  contains the total silica, that is, the silica that was added plus that contained in the sample. The total silica is then evaporated as usual with an excess of HFl plus 5 drops of conc.  $\text{H}_2\text{SO}_4$ . The HFl should be added very cautiously, and in small installments, to prevent loss by spraying during the formation of the volatile silicon fluoride. The silica is then determined by the loss of weight after the removal of the excess of the two acids as in steels. Any

residue remaining in the crucible after the removal of the silica may contain some calcium, iron, etc., and is fused with a little sodium carbonate, dissolved in HCl and added to the filtrate from  $M''$ .

*Ca, Mg, Ba, Fe and Al* are now all in solution in the filtrate just mentioned. The first step is to remove any barium present by adding to the solution 2 c.c. of conc. sulphuric acid diluted with 600 c.c. of water. Any precipitate formed by the addition of the very dilute sulphuric acid is filtered off, ignited and weighed as barium sulphate. The filtrate and washings from the barium sulphate are then analyzed for Ca, Mg, iron and aluminum as described for limestone, beginning at the point where these elements are all in solution and free of silica. (See page 357.)

*Blanks.* It is very necessary to run blanks by fusing 3 grams of the same lot of precipitated silica as used in the decomposition of the spar with 10 grams, each, of the sodium and potassium carbonates. The melt is dissolved out in water and then put through all of the operations given in the method. The silica, iron, calcium, magnesium and aluminum so found are deducted from the amounts of these elements found in the analysis of the sample. These blank analyses should be made in duplicate, as should the analysis of the spar, also.

*Lead.* Dissolve 0.9 and 1.0 gram of the sample in a mixture of 20 c.c. of conc.  $HNO_3$  and 10 c.c. of conc. HCl. If the spar is high in  $CaF_2$  it will dissolve almost completely in this mixture. Heat until all spraying is over and evaporate to moist dryness; redissolve in 20 c.c. of conc. nitric acid, dilute, filter, wash with dilute nitric acid, and evaporate the filtrate and washings to 10 c.c. Add 75 c.c. of conc. HCl and evaporate to 15 c.c. Dilute with water to about 100 c.c. Make the diluted solution just neutral with ammonia; add 4 drops of HCl and pass  $H_2S$  through the hot solution until the black precipitate of lead sulphide settles well. Filter off the lead sulphide and wash it with  $H_2S$  water. Pass  $H_2S$  through the filtrate and washings to make certain that all of the lead has been precipitated. The lead sulphide is dissolved in 50 c.c. of 1.20 nitric acid and its solution

is evaporated to heavy fumes with 75 c.c. of 1 : 3 sulphuric acid, in a porcelain dish. Cool, dissolve as far as possible with 200 c.c. of water and one-third this amount of alcohol. Allow the lead sulphate to settle for several hours before filtering; filter off the lead sulphate and wash it with a mixture of 2 parts of water and 1 part of alcohol. Burn the residue at a very low heat in a *porcelain* crucible until the paper is all gone. Cool the white residue and moisten it with a drop or two of  $H_2SO_4$  and ignite the residue again at a dull red heat.

The weight so obtained is multiplied by 0.6831 to reduce to the metallic basis. If the sulphur found is reported as such then the lead can be conveniently reported as metal. The lead however usually is present as the sulphide.

*Sulphur.* The author uses the carbonate and nitre fusion, melting the spar with 20 grams of carbonate of soda and 4 grams of nitre. The analysis is then finished as in ferro-vanadium high in silicon (see page 17 near the bottom of the page). There is no reason why the sulphur could not be obtained by fusing the mineral in 15 grams of peroxide and then dissolving out the melt in water. The water solution could be acidulated with a considerable excess of HCl and the analysis finished as in the carbonate and nitre fusion.

In either method blanks should be run through all the operations and deducted.

*Carbon Dioxide.* Ignite 1 gram of the sample in the electric combustion furnace in a stream of oxygen for one hour, as in the determination of carbon in steel. The carbon dioxide is usually combined with calcium, as carbonate, in the mineral.

#### APPROXIMATE METHOD.

The usual approximate method is to attack the spar with acetic acid. The author proceeds as follows (he regards the approximate method accurate enough for all technical purposes): Moisten the finely ground spar to a thin paste with water, add 20 c.c. of glacial acetic acid and evaporate to dryness on the water bath in a porcelain dish. To the dry residue add 50 c.c.

of water; stir, boil a few minutes; add ashless paper pulp; mix again, filter and wash with hot water, obtaining residue *R* on the filter and filtrate and washings *F*. The residue *R* contains all of the  $\text{CaF}_2$ , silica and the main portion of the iron, aluminum and lead. Barium if present as sulphate would be mainly in *R*.

The filtrate and washings from *R* contain calcium, magnesium and some of the iron and aluminum, and are analyzed for these elements as in limestone (see page 357). If lead is present some of it will also be in this filtrate and should be first removed by  $\text{H}_2\text{S}$  precipitation of the hot, faintly acid solution. The lead sulphide is washed with  $\text{H}_2\text{S}$  water and the filtrate and washings are evaporated low to remove the excess of  $\text{H}_2\text{S}$ , adding some potassium chlorate to oxidize the iron, at the beginning of the evaporation. The amount of lead found at this point is only a small portion of the total amount of the lead present; at least, this is the case in the samples containing lead as galena.

*Silica and Calcium Fluoride.* The residue *R* is ignited at a low red heat in a weighed platinum crucible, cooled and weighed. 20 c.c. of c.p. HFl are added to *R* after the weighing. Evaporation to dryness removes the silica. The remainder in the crucible is then heated to lowest redness, cooled, weighed again, and the loss of weight due to the evaporation and ignition is calculated as silica. 3 c.c. of conc.  $\text{H}_2\text{SO}_4$  are dropped into the crucible and the contents of the latter are taken to dryness; ignited at a low red heat, cooled and weighed as calcium sulphate ( $\text{CaSO}_4$ ). The calcium sulphate so found is calculated to calcium fluoride after deducting from it any Ba, Pb, Fe and Al found as given below.

Add 15 c.c. of conc. HCl to the weighed calcium sulphate and boil it until the sulphate either dissolves to a clear solution after 20 minutes slow boiling, or there remains some white insoluble residue which would indicate the presence of barium sulphate. If such a residue be found, then dilute the solution to 200 c.c. and let it stand for several hours to permit the barium sulphate to settle. Filter it out; wash it with water; ignite, cool, weigh,

and deduct it from the weight of the calcium sulphate. The filtrate and washings from the barium sulphate are diluted to 400 c.c. and  $H_2S$  is passed for an hour and the solution is then permitted to stand for several hours to give the precipitate of  $PbS$  time to separate out. If there be sulphide of lead in the spar (usually in the form of galena), then some of it will have been counted as calcium sulphate. The lead sulphide is burned at a very low red heat in a porcelain crucible, moistened with a few drops of conc. sulphuric acid and the latter is evaporated. The residue is burned at a low red heat, weighed and the weight is then deducted from that of the calcium sulphate. The filtrate and washings from the lead sulphide are evaporated to dryness with a gram or two of potassium chlorate and analyzed for any small amounts of iron and aluminum that may be present in this part of the analysis; that is, the small residue in the evaporating dish is dissolved in 10 c.c. of HCl, precipitated with a slight excess of ammonia, the small precipitate of iron and aluminum hydroxides are filtered out, washed, weighed and the weight also deducted from the weight of main calcium sulphate. The main calcium sulphate as stated, after these deductions, is then calculated to the total calcium fluoride. These small portions of the Fe and Al are also added to the main oxides of iron and aluminum found in  $F$ . The main filtrate  $F$  contains all of the calcium and magnesium *not* existing in the mineral as fluorides; also the remainder of the lead if any is present and the main portion of the iron and aluminum. The lead is removed first, after acidulating  $F$  with a slight excess of HCl to prevent the coprecipitation of any iron, by means of hydrogen sulphide. The filtrate and washings from the lead sulphide are evaporated to dryness with an excess of at least 20 c.c. of conc. HCl and 1 gram of chlorate. The dry residue is then taken up with 10 c.c. of 1 : 1 HCl and the iron, aluminum, calcium and magnesium in the solution are determined as in limestone. As stated, the lead, iron and aluminum found here are added to any portions of these elements found in the filtrate from the hydrochloric solution of the calcium sulphate.

**CALCULATIONS.**

In the *exact method*, the calcium required in the calcium fluoride found is deducted from the *total* calcium found. Any calcium remaining is usually calculated to calcium carbonate. The author prefers for the sake of simplicity to calculate to calcium oxide the calcium found in excess of that necessary to produce the calcium fluoride; and report the carbon dioxide found as such instead attempting to distribute it as carbonate. In the same way the sulphur found is reported as such instead of entering into a tedious computation for the purpose of calculating a part of it to lead sulphide and any remaining sulphur to sulphide of iron. Similarly the oxides of iron and aluminum obtained are reported as oxides. For commercial and technical purposes this seems the logical procedure, and entirely answers purposes of the iron and steel metallurgist. In harmony with the reporting of the sulphur as such, the lead found is recorded as metal.

**CALCULATION OF THE CALCIUM EXISTING AS CAO BY THE EXACT METHOD.**

Suppose that 83.46 per cent of  $\text{CaF}_2$  were found. Then in one gram of the sample there would be 0.8346 gram of calcium fluoride. Further, in one gram of this sample there was found a total of 0.6956 gram of calcium oxide in the filtrate from *M''*, page 378; then as calcium fluoride is converted to its equivalent weight of calcium oxide by the factor 0.7182 we have 0.8346 multiplied by 0.7182 or 0.5994 gram of calcium oxide coming from the calcium in the calcium fluoride. This is deducted from the total calcium oxide; 0.6956 minus 0.5994, or 0.0962 gram of calcium oxide to be reported as such, being 9.62 per cent.

**CALCULATION OF  $\text{CaSO}_4$  TO  $\text{CaF}_2$  IN THE APPROXIMATE METHOD.**

The calcium sulphate found is multiplied by the factor 0.5735 to obtain the equivalent weight of calcium fluoride.

## SOME ANALYSES OF FLUORSPAR.

Sample of Fairview Gravel.

	Approximate Method. Per Cent.	Exact Method. Per Cent.
Calcium fluoride.....	83.70	83.46
Silica.....	2.92	3.20
Oxides of iron and aluminum.....	3.16	3.20
Calcium oxide.....	9.40	9.61
Sulphur.....	0.016	0.016

Sample of Fluorspar Gravel Containing Sulphide of Lead.

	Approximate Method. Per Cent.	Exact Method. Per Cent.
Calcium fluoride.....	84.24	84.36
Silica.....	5.44	5.79
Oxides of iron and aluminum.....	1.32	1.41
Calcium oxide.....	1.83	1.90
Carbon dioxide.....	2.20	2.20
Sulphur.....	0.92	0.92
Metallic lead.....	2.00	2.00
Moisture.....	0.35	0.35

Selected Sample by the Approximate Method.

	Per Cent.		Per Cent.
Calcium fluoride.....	97.58	Oxides of iron, etc.....	0.77
Silica.....	0.20	Oxide of calcium.....	0.62

## CHAPTER XIX.

### PART I.

#### THE TESTING OF LUBRICATING OILS.

As the steel works' chemist is frequently required to report on the lubricants used about the plant, a brief outline of the more important tests may save the busy reader of this book much delving into the vast amount of literature written on this subject. The tests about to be described constitute all that the mechanical engineering department of a large works usually cares to know, or asks for. If the reader wishes to inform himself further, he can consult the writings of Lewkowitch, Benedict, Gill and others.

##### SAPONIFICATION NUMBER.

This test is a direct index of the proportion of animal matter in the lubricant for the reason that mineral oil (usually present in most of the oils used for lubricating) has no saponification value. The saponification number simply means that one gram of the sample tested requires that many milligrams of potassium hydroxide to combine with (saponify) the fatty acids present in it. The test is also known as the Koettstorfer's value.

##### METHOD.

Weigh 1 to 2 grams of the oil or lubricant into a 250 c.c. conical flask. Place also in the flask 25 c.c. of half normal potassium hydroxide. Insert a stopper carrying a return condenser firmly in the neck of the flask. Turn a current of water into the condenser and start to heat the flask on a water bath. (See photo No. 27.) Some operators add 20 c.c. of ether to the contents of the flask before putting in the condenser. Heat the flask on the water bath for one hour. Then shut off the heat, turn off the water, cool, add several drops of phenolphthaleine indicator

and drop in from a burette half-normal HCl until the pinkish color or shade given to the solution by the indicator just disappears. The number of c.c. of N/2 KOH added, less the number of c.c. of HCl required to discharge the pinkish color produced by the KOH, multiplied by the factor 28.05 (1 c.c. of N/2 KOH contains 28.05 mgs. of KOH) and divided by the weight of the



PHOTO 27.

oil taken gives the saponification number of the sample. In weighing the oil place the tared flask on the balance pan and drop in some of the sample from a pipette until about the desired weight has been put in the flask. Then weigh the oil exactly.

When titrating the oil with N/2 HCl use alcohol to wash down the sides of the flask, as water is liable to cloud the solution. To check the operations place 25 c.c. of the N/2 KOH in the cone flask together with the 20 c.c. of ether. Connect the condenser and heat the flask for one hour in the water bath, cool and titrate with the N/2 HCl. Any KOH that may have

been so used is deducted from the apparent amount used by the sample, before calculating the saponification number as given above.

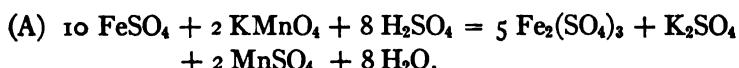
A convenient standard for checking the operator's work is the purest rapeseed oil. A very pure sample obtained by the writer gave a saponification value of 185. A German rape oil known as double refined was found to be 182 in saponification. Pure lard oil is given as 195. These pure oil standards should be kept in a cool dark cupboard, in sealed bottles, when not in use.

#### THE PREPARATION OF HALF-NORMAL (N/2) HCl AND HALF-NORMAL KOH.

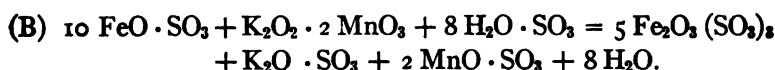
A normal solution is usually defined as the hydrogen gram equivalent of the active substance dissolved in a liter volume. The author would like to offer the following definition which may seem long drawn out but more explanatory:

A normal solution is the gram molecular weight of the reacting substance dissolved in a liter volume, or that fraction of its gram molecular weight dissolved in a liter volume which is the equivalent of the gram atomic weight of hydrogen. The required fraction of the gram molecular weight may be different for the same compound, depending on the nature of the reaction for which the normal solution is to be used.

The first requisite is then to write the equation and from it decide whether the full molecular weight in grams or only a fraction of it is needed to meet the conditions of normal solution. Suppose the normal solution of permanganate of potassium is desired for the oxidation of ferrous sulphate, according to the equation:



or



By equation (B) we see how the oxidation expressed by (A) takes place: The ferrous oxide united to the sulphuric radical and containing 10 atoms of oxygen becomes ferric oxide, still united to the sulphuric radical, and gains 5 atoms of oxygen. This gain comes from the permanganate as by equation (B) the potassium peroxide part of the permanganate loses 1 atom of its oxygen to the ferrous sulphate, becoming potassium sulphate; and the two parts of manganic trioxide give up four atoms of oxygen to the ferrous sulphate, and become 2 molecules of manganese sulphate. Hence we have permanganate equivalent to 5 atoms of divalent oxygen or 10 atoms of monavalent hydrogen; therefore 2 molecules of the permanganate being equivalent to 10 atoms of hydrogen then  $\frac{2}{10}$ ths or  $\frac{1}{5}$ th of a gram molecule of the  $\text{KMnO}_4$  will be the equivalent of the gram atom of hydrogen. This makes it necessary to weigh  $\frac{1}{5}$ th of 158.03 or 31.6 grams of the  $\text{KMnO}_4$ , dissolving the same in a liter volume.

A normal solution of the ferrous sulphate: It has been seen that the sulphate of iron has taken up 5 atoms of oxygen which are equivalent to 10 atoms of hydrogen, hence, since 10 molecules of the ferrous sulphate are equivalent to 10 atoms of hydrogen, then 1 molecule of the sulphate is equivalent to 1 atom of hydrogen. It will be fulfilling the definition if 278 grams of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  are dissolved in a liter volume, or the entire gram molecule.

An example of a normal solution for a precipitation reaction is afforded by the following:  $\text{H}_2\text{SO}_4 + \text{BaCl}_2 = \text{BaSO}_4 + 2\text{HCl}$ . In this equation the active sulphuric acid molecule precipitates the divalent barium atom which is equivalent to 2 atoms of the monavalent hydrogen atom, therefore  $\frac{1}{2}$  the gram-molecular weight of the sulphuric acid, or 49.04 grams of the 100 per cent acid or its equivalent in a dilution, in a liter volume constitutes its normal solution.

(C) This brings one to the neutralization normal, or half-normal solution:  $\text{HCl} + \text{KOH} = \text{KCl} + \text{H}_2\text{O}$ . In this reaction whether it is desired to consider the normal solution for the potassium hydroxide or the hydrochloric acid it is an example of one molecule reacting with a monavalent atom. In either case

the entire gram molecule would be required in the liter volume or one-half this amount for the half-normal solution, also in a liter volume. This would be 36.47 grams of the HCl and 56.11 grams of the KOH in a liter volume for the normal solution, or 18.23 grams of HCl and 28.05 grams of KOH dissolved in a liter volume for the half-normal solution ( $N/2$ ) of these salts.

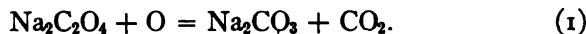
*Half-normal HCl.*

As the hydrochloric solution will remain constant, 7 liters are prepared as follows: 350 c.c. of about 1.20 specific gravity acid are diluted to 7000 c.c. with water and well mixed. The acidity is then tested against pure sodium carbonate prepared from c.p. sodium oxalate which can be obtained to the best advantage from the U. S. Bureau of Standards.

Weigh 1 gram of the standard oxalate into a platinum crucible and gently ignite until it is charred and then raise the heat until it is pure white but do not heat it above redness. Dissolve the sodium carbonate thus formed in a little water and transfer it with great care to a 250 c.c. cone flask. Add 1 or 2 drops of methyl orange solution and titrate it with some of the above HCl solution until one drop of the acid just turns the fluid in the cone flask pink. The reaction is as follows:



The sodium oxalate on ignition is decomposed to sodium carbonate in the manner shown by the equation,



By (1) one molecule of sodium oxalate yields 1 molecule of sodium carbonate and by (2) we see that 1 molecule of sodium carbonate is also equivalent to 2 molecules of hydrochloric acid. Or in terms of equivalent weights, 134 parts of sodium oxalate yield 106 parts of sodium carbonate, which require 72.94 parts of HCl (2 HCl) for neutralization. 1 gram of sodium oxalate will give 106/134ths of a gram of sodium

carbonate, or 0.791 gram. Suppose that the trial titration of 7 liters of HCl showed that 0.791 gram of sodium carbonate required 25.0 c.c. of this HCl to give a pink with the methyl orange. By (2) we have seen that 72.94 parts by weight of HCl unite with 106 parts of sodium carbonate or 1.4532 grams of  $\text{Na}_2\text{CO}_3$  equal 1 gram of HCl. N/2 HCl according to (C) contains 18.23 grams of HCl to the liter, therefore 1 c.c. of N/2 HCl equals  $18.23 \times 1.4532 \div 1000$  grams of sodium carbonate, or 0.02650 gram of  $\text{Na}_2\text{CO}_3$ . As an average of several titrations it was found that 25 c.c. of the solution of HCl being tested neutralized 0.791 gram of  $\text{Na}_2\text{CO}_3$ , hence 1 c.c. of this acid equals  $0.791 \text{ gram} \div 25$ , or 0.03164 gram of  $\text{Na}_2\text{CO}_3$ . As 1 c.c. of N/2 HCl should equal 0.02650 gram of  $\text{Na}_2\text{CO}_3$  then 1 c.c. of the acid being tested should be diluted in volume as many times as 0.0265 is contained in 0.03164, or 1.194 times. Suppose after making the trial titrations there remains exactly 6800 c.c. of the HCl, then this solution should be diluted to  $6800 \times 1.194$  c.c., or to 8119 c.c., when it should be an exact N/2 normal solution.

In general divide any number of c.c. of the acid being standardized into the amount of sodium carbonate that it will exactly neutralize; divide the result by 0.02650 and then multiply this last quotient by the exact number of c.c. of the acid remaining. This will give the volume to which the remaining acid must be diluted to make it of N/2 strength.

#### THE PREPARATION OF N/2 KOH.

Weigh about 40 grams of KOH, marked purified by alcohol, into a glass stoppered bottle and dissolve it in a liter of ethyl alcohol that has been distilled with some KOH.

This distillation can be accomplished by placing the alcohol and KOH in a boiling flask, in boiling water and connecting the same with a Bunsen condenser. The distillate is then used as above. In the alcoholic solution a gram or two of barium hydroxide are also placed to remove any carbonate present in

the KOH solution. It is then allowed to settle for twelve hours, when the clear liquid is siphoned off, leaving all of the cloudy portion behind. This clear portion is diluted to one liter and well mixed in a glass stoppered volumetric flask. The redistilled alcohol is used for this dilution also. Exactly 50 c.c. of this KOH are withdrawn from the 1000 c.c., and 25 c.c. of it are titrated with the N/2 HCl. Suppose it is found that 28.7 c.c. of the N/2 HCl are required to just turn the 25 c.c. of the KOH pink; then 1 c.c. of the KOH equals  $28.7 \div 25$ , or 1.148 c.c. of the HCl. Hence the 950 c.c. of the KOH that remain must be diluted to  $950 \times 1.148$ , or 1090 c.c. to make them the equivalent of the N/2 HCl and therefore an N/2 KOH solution. This dilution is made as in the others with the alcohol that has been distilled in the presence of KOH.

#### CALCULATIONS.

In actual work the N/2 KOH does not remain for any length of time exactly of N/2 strength so it is more convenient to determine its exact relation to the N/2 HCl, which latter acid should remain unchanged. Suppose it is found as a result of the mean of several titrations of the HCl against the KOH that the 29.2 c.c. N/2 HCl equal 30 c.c. of the KOH. Since 1 c.c. of N/2 HCl reacts with exactly 28.05 mgs. of KOH, 1 c.c. of the KOH solution being tested is equivalent to  $28.05 \times 29.2 \div 30$  c.c., or 27.30 mgs. of KOH, which value can then be used at that time, instead of the factor 28.05 which can be used only when the KOH is exactly normal.

#### FLASH AND FIRE TESTS.

The writer uses the open fire tester of Tagliabue.

Place a bed of chip graphite in the bottom of the tester. Fill the reservoir with the oil to within  $\frac{1}{4}$  inch of the top and raise the temperature at the rate of 15 degrees per minute; try for a small flash of flame across the surface of the oil every 7 degrees. After getting the flash make note of the temperature and continue

to raise the same until the oil takes fire and note this temperature which is the fire test. For an igniter use a small glass jet in a rubber hose connection so that the flame coming from the jet is not more than one-eighth of an inch long. In using this small igniting flame draw it across the diameter of the surface of the oil and keep the little flame on a level with the top of the tester, making sure that the jet does not touch the oil at any time. Keep the tester surrounded with a sheet iron cylinder during the testing to protect it from draughts. This test should be always carried out under exactly the same conditions or the results will be discordant. When the burning test has been completed smother the flame at once with the cover that goes with the instrument as this serves to put out the flame and makes the tester easier to clean for the next sample.

Consult Technical paper No. 49, Dept. of Interior, Bureau of Mines, by Allen and Crossfield, 1913, on the Flash Point of Oils.

#### COLD TEST.

Fill a 4-ounce wide neck glass stoppered bottle about half full of the oil and place it in a freezing mixture consisting of 2 parts of ice and 1 part of salt, which can be kept in a small can wrapped with asbestos. After the oil is solid, let it stand in the mixture for about an hour. Then take out the bottle and place a thermometer in it and stir with the thermometer until the oil will just flow from one end of the bottle to the other. The cold test is that temperature at which the oil will just flow.

#### TEST FOR FREE ACID.

This test is usually reported in grams of free oleic acid and N/6 KOH is used for the purpose, 1 c.c. of which is equal to 0.047 gram of free oleic acid. Weigh 8 to 10 grams of the oil, accurately, into a 250 c.c. cone flask. Add 100 c.c. of the redistilled alcohol prepared as given under Saponification. Put the flask in a water bath and bring the contents quickly to just 60° C. Then take the flask off the bath at once and titrate with the

N/6 KOH until the first pink color just spreads through the test. Do not carry the titration any further or the result will be too high due to a certain amount of saponification taking place. The number of c.c. required to produce this first pink, multiplied by 0.047 and divided by the weight taken gives the amount of free oleic acid per gram which is then reported in percentage.

The alcohol used in these tests can be recovered by distilling off the same after the tests are completed. Add some quick-lime to the fluid before distilling off the alcohol to remove any water.

#### VISCOSITY.

Any of the viscosimeters on the market can be used for this test. The writer also uses the Tagliabue instrument for this work. Full directions go with these instruments so that but a brief hint or two is all that is necessary. For testing the oil at 70 degrees attach the nipple marked 70 degrees to the outlet and be sure that the oil has no dirt in it. If the room temperature is above 70 degrees pour 90 c.c. of the oil into the container and just as soon as the oil reaches the required temperature allow 70 c.c. to pass through the nipple, timing its flow in seconds with a stop watch. The number of seconds required multiplied by two gives the viscosity.

To test oil at 212 degrees water is brought to that temperature in the boiler of the viscosimeter, and the steam coming from the water passes through the steam jacket of the instrument which surrounds the oil container. 80 c.c. of the sample which has already been heated to 22 degrees or more are now placed in the oil container, and when the 212 degrees are reached in the oil, as shown by the thermometer that goes with the instrument, 60 c.c. of the oil are withdrawn through the nipple marked 212 degrees and the time of its flow is recorded in seconds with the stop watch. The seconds required multiplied by two give the viscosity.

The Engler viscosimeter refers all viscosity values to the same figures obtained by passing distilled water through his instrument. The figures obtained on the oil tested are divided

by those gotten from water in the same way. This gives what he terms the specific viscosity.

The viscosimeter should be cleaned with ether after each test to prevent any gummy coating forming on the walls of the nipples which would impair the accuracy of the instrument. The viscosity of water for this instrument used in this laboratory was found to be 40 at 70 degrees and 75 at 212 degrees.

#### SPECIFIC GRAVITY.

For the determination of specific gravity the Eichorn picnometer is used. Cool the oil to 60° F. and fill the little bulb slowly with the oil so that no air bubbles enter with the oil, as the presence of air in the reservoir renders the result entirely inaccurate. Hold the picnometer at about a 70 degree angle when filling it so that the bubbles may be worked out to a better advantage. When the bulb is entirely full of the oil, and free of air, stopper it, wipe it free of oil, place it in a cylinder of water which is at 60° F. and read the specific gravity from the graduation of the instrument that is tangent to the meniscus curve of the surface of the water.

#### RESULTS OF SOME OIL TESTS.

Cylinder Oil.							
	Acid Test.	Flash.	Fire.	Viscosity, 212° F.	Sp. Grav.	Sap. Val.	Cold Test.
2/7/12.	Per Cent	Degrees	Degrees				Degrees
United Cylinder oil.....	0.168	546	628	153	0.895	20.53	40
Capitol.....	0.279	555	630	184	0.89	22.61	37
Dark crescent.....	0.232	566	646	197	0.898	22.24	36
3/18/12.							
Capitol.....	0.126	505	558	161	0.914	18.30	39
8/13/12.							
Special 600.....	0.00406	492	526	139	0.910	22.45	26
High standard.....	0.00215	508	552	185	0.918	17.84	30
No. 1 Oil City Oil.....	0.00110	590	642	189	0.890	16.93	37
No. 2 Oil City Oil.....	0.00108	555	622	162	0.884	16.45	32
.....	0.00223	505	570	148	0.880	21.25	42
.....	0.003	462	522	125	0.882	8.98	44
Capitol cylinder oil....	0.002	551	618	178	0.893	6.41	41

## Lubricating Oil.

	Acid Test.	Flash.	Fire.	Viscos- ity, 212° F.	Sp. Grav.	Sapon. Value.	Cold Test.
Brook's.....	o. 144	558	628	160	o. 892	17.60	35
Young's.....	o. 113	530	588	134	o. 895	30.24	46
Voegley.....	o. 258	546	624	185	o. 866	21.78	40
W. V. Lub.....	o. 139	357	399	102	o. 884	8.029	15

## MISCELLANEOUS OILS.

	Acid Test.	Flash.	Fire.	Viscos- ity, 212° F.	Sp. Grav. 60° F.	Cold Test.	Sap. Val.	
8/22/12.								
Roll oil.....	o. 016	404	459	187	o. 870	17° F.	20.12	
Tempering oil.....	o. 0038	488	552	142	o. 860	35.6° F.	2.82	
Torch oil.....	.....	205	229	50	o. 844	.....	5.5	
3/27/11.								
Mineral lard oil cutting oil.....				Sap. Value.	Viscos- ity at 70° F.	Viscos- ity at 212° F.	Flash Point.	Fire Test.
				61	183	92	384	452

## SOME SPECIFICATIONS FOR OILS.

*Engine oils.*

1. Flashing point above 400° F.
2. It must be a pure mineral hydrocarbon oil, free from adulteration.
3. Its specific gravity must be between 26° and 30° Baumé.
4. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette) must be, when determined at 80° F., not less than 2.5.
5. The oil must be free from acids, sulphur compounds or any other corrosive substances, and free from dirt or any other gritty material.

*Heavy Dark Engine Oil.*

1. Flashing point above 45° F.
2. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette), when determined at 80° F., must not be less than 2.5.
3. The oil must be free from all sulphur compounds, acid or any other corrosive substances of any kind, and free from dirt or any gritty substances.
4. Its specific gravity must be between 26° and 30° Baumé.

*Cylinder Oil.*

1. It must have a flashing point of not less than 55° F.
2. Its specific gravity must be between 25° and 26° Baumé.
3. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette), when determined at 330° F., must not be less than 1.25.
4. It must contain no saponifiable animal oil, and be a pure mineral hydrocarbon oil, free from adulterations.
5. The oil must be free from sulphur compounds, acids or any other corrosive substances of any kind, and must be free from dirt or any gritty substances.

*Journal and Roll Neck Grease.*

1. It must be free from all dirt and grit of any kind, acid or corrosive substances.
2. It must be absolutely neutral in reaction and free from metallic oxides, other than lime.

*Torch Oil.*

1. It must have a flashing point of not less than 125° F.
2. It must show a fire test not below 150° F.
3. Its specific gravity must be between 44° and 48° Baumé at 60° F.
4. It must not become cloudy when cooled at 0° F.
5. This oil must be pure petroleum oil, free from dirt, grit, lumps, water, etc.

*Paraffine Oil.*

1. This oil must be neutral in reaction, free from all dirt or similar substances, and may have a flashing point as low as 200° F. It must be pure petroleum oil.
2. Its viscosity (compared with water at 60° F., using a P.R.R. standard 100 c.c. pipette), when determined at 60° F., should not be less than 1.2.

*Screw Cutting Oil.*

1. This oil shall consist of paraffine oil of about 27° Baumé gravity compounded with not less than 25 per cent by weight of fat oil, cotton seed preferred.
2. The compounded oil shall have a flashing point not below 300° F. and a burning point not above 425° F.

*Fish Oil.*

1. It must have a flashing point of not lower than 525° F.
2. It must congeal at 43° F.
3. It must be free from soaps of any kind.
4. It must have a specific gravity of 21° Baumé.
5. It must be free from dirt and impurities.

Barrels must be in good condition, and should any barrel contain water, dirt or other impurities it will be rejected.

NOTE. The foregoing specifications follow very closely those gotten out by the Philadelphia & Reading R. R. under Robt. Job.

**VISCOSITY BY THE UNIVERSAL STANDARD SAYBOLT  
VISCOMETER.**

The following viscosity figures were recently recommended to the author by a chemist of much experience in the manufacture of lubricants:

Engine oil at 100° F., 150 to 200 viscosity; average 160 to 180.

Heavy, dark engine oil at 130° F., 175 to 250 viscosity; average 200.

Cylinder oil at 212° F., 150 to 200 viscosity; average 160 to 170.

Paraffine oil at 100° F., 110 to 150; for light work, 100, and for heavy work, 150 viscosity.

## CHAPTER XIX.

### PART II.

#### THE TESTING OF COAL.

*External Moisture.* By this term is meant the rain, snow, or mine, or barge water adhering to the surfaces of the coal. For this determination samples should be put at once into Mason jars supplied with screw tops and rubber washers or gaskets. The jars should be filled at the place of sampling and the tops screwed down, tightly, on the rubber. The jars can then be taken to the laboratory and allowed to attain the room temperature and weighed without opening them. After getting this weight, the jars are opened and the contents are spread out in thin layers, taking care that this operation is performed without the smallest loss of the weighed coal. The opened jars are placed in a bath of hot air to dry. The rubbers are removed and marked the same as their respective jars during the drying of the latter at a temperature of about 80° C. The contents of the jars are also labeled and are dried, without any crushing, at a temperature of 100° C. for several hours until all evidences of external dampness is gone and the fines in the samples have a tendency to be dusty. The tests are then returned to their respective containers; the rubbers and tops are also returned to their jars. The jars and their dried contents are again weighed after regaining the room temperature. The dry, empty jars with caps and rubbers on were also weighed in the meantime. The weight of the jars and the wet contents less the weight of the jars and the dry contents equals the weight of external moisture. The weight of the external moisture multiplied by 100 and divided by the weight of the corresponding jar and wet contents, from which has been deducted the weight of the dry empty jar, constitutes the per cent of external moisture. All weights referred

to are taken with the caps and rubbers on the jars and are made on a torsion balance. This balance is of 10 kilos capacity and sensitive to a tenth of a gram. For these tests large samples are taken, from 1 to 2 pounds.

*Internal Moisture.* The sample after being used for the determination of the external moisture is crushed to 100 mesh or finer and 1 gram of the powdered coal is dried for one hour at 105° C. The loss of weight constitutes the internal moisture which is reported in percentage. The sample is dried in a 20 c.c. platinum crucible.

*Volatile Matter.* Place the crucible containing the sample on which the internal moisture determination was made in a ni-chrome triangle supported 8 cm. above the top of a Bunsen burner and play a flame 10 cm. high back and forth across the bottom of the crucible which is covered with a tightly fitting lid. Continue this heating for 4 minutes. Then place the burner directly under the crucible with the flame stationary and increase the length of the flame to 20 cm. Continue to heat for 7 minutes more. Cool in a desiccator and weigh. The loss of weight constitutes the volatile matter.

The Committee on Coal Analysis of the American Society for Testing Materials and the American Chemical Society recommend that the volatile matter be determined in a 10 gram platinum crucible, using a capsule lid, that is, one that fits inside the crucible. The crucible and its one gram sample can then be placed in a muffle heated to 950° C. and maintained at this temperature for 7 minutes. The author would prefer to use an electrically heated muffle furnace\* which every laboratory should have, without fail, and can make at a low cost for this purpose. See Making and Repairing of Laboratory Electric Furnaces, page 419. The crucible is placed on a ni-chrome triangle support bent so as to keep the bottom of the crucible clear of the floor of the furnace.

*Fixed Carbon and Ash.* The residue remaining in the crucible after the determination of the volatile matter is heated to a dull red and maintained at this heat until all carbon is burned away.

\* The electric muffle is ventilated by a regulated stream of air drawn from the compressed air pipe.

The operation can be facilitated by supporting the crucible in a slanting position with the lid only partly covering it. Also occasional stirring of the mass in the crucible, using great care to prevent loss of the ash, will expedite the removal of the carbon. When the ash has assumed a uniform grey or reddish color free of all black material, the crucible is transferred to a desiccator, cooled and weighed. The loss of weight due to this removal of carbon is calculated to percentage as fixed carbon, on a basis of one gram.

The ash found in the fixed carbon determination can be calculated as such to percentage or the ash can be gotten on a separate one gram sample. The freshly weighed sample is at first smoked off on a Bunsen burner as described in the determination of the volatile matter. The crucible is then raised to a dull red heat after all smoking is over and the heating is continued as already described. The extensive preliminary report of the committee above mentioned can be found in the Journal of Industrial and Engineering Chemistry, Vol. 5, No. 6, pages 517-528.

*Heat Units.* Any of the well known calorimeters can be used for this work. As the details of the operations of the instruments are always furnished with the latter, it seems quite unnecessary to repeat them here. The author would recommend that operator check his work and the instrument against some convenient material of known heat units. For this work the writer has a standard coal powder on which the heat units were determined by the U. S. Bureau of Standards and a sample of the standard benzoic acid which is also furnished by the same institution for a small fee. The checking should be done at frequent intervals during the operation of the calorimeter.

*Sulphur.* Grind together in an agate mortar 4 grams of magnesia and 2 grams of sodium carbonate until an intimate mixture of these materials is obtained. Mix thoroughly with four-fifths of this mixture 1 gram of the finely powdered coal in a platinum or porcelain crucible. Then put the other one-fifth of the mixture as a layer on top of the mixture of coal

powder, magnesia and sodium carbonate. Place the crucible in an inclined position over the low flame of a Bunsen burner. Move the flame slowly back and forth under the crucible until it is very gradually brought to a low red heat on the bottom, and the mixture glows faintly under the top layer, as can be ascertained by giving the mass a slight stir with a ni-chrome wire. Continue this low heating until all black due to carbon is gone. Stir the mass at intervals.

Transfer the residue in the crucible, when the carbon is gone, to a casserole. Rinse out the crucible with about 40 c.c. of water, adding the rinsings to the residue in the casserole. Add 70 c.c. of bromine water to the casserole, cover it with a watch glass, boil 10 minutes, remove the cover, add 50 c.c. of conc. HCl and evaporate to dryness. Cool, add 20 c.c. of conc. HCl, heat, add 100 c.c. of water, filter out any insoluble matter and wash with dilute HCl. Dilute the filtrate and washings to 300 c.c. Heat to boiling and add 25 c.c. of a saturated solution of barium chloride diluted with 75 c.c. of water. Let the barium sulphate settle for several hours, preferably over night. Finish as in gravimetric sulphur in steels.

For a check the operator can carry through the factor weight as recommended by the before mentioned committee. The above is a modified form of the Eschka method. Blanks should be carried through all of the above operations and deducted.

For a check method 1 gram of the powdered coal can be fused in the calorimeter bomb with sodium peroxide and potassium chlorate per directions given with the calorimeter. Also  $\frac{1}{2}$  gram of coal can be fused in a platinum crucible with a mixture of 15 grams of sodium carbonate and 5 grams of potassium nitrate, dissolved out in water, transferred to a casserole, acidulated with HCl and finished as in the Eschka method. A further check method is to fuse 0.5 gram of the powdered coal with a mixture of 15 grams of sodium peroxide and 7.5 grams of sodium carbonate in an iron crucible. The melt is dissolved out in water, acidulated with HCl and finished as in the other methods.

The barium sulphate, obtained by any of the methods given, must be moistened with a few drops of dilute sulphuric acid after it has been ignited free of carbon. It is then ignited again to free it of the excess of the sulphuric acid. This insures against the presence of barium sulphite due to the reducing action of the burning filter paper.

*Phosphorus.* Obtain the ash from 1.63 grams of the coal by burning the same on a low flame in a 20 gram platinum crucible. Fuse the ash with 20 times its weight of sodium carbonate and 0.100 gram of niter. Dissolve out the fusion with water, and transfer it to a casserole and acidulate with HCl, keeping the casserole covered to avoid loss. Heat until all spraying is over; evaporate to dryness, cool, redissolve by first heating with 10 c.c. of conc. HCl. Add 50 c.c. of water. Heat, filter, add a few drops of ferric chloride solution unless there is enough iron present to give a red precipitate with ammonia in the filtrate and washings. Wash the ammonia precipitate a few times with water and then dissolve it off the filter with 20 c.c. of 1.20 nitric acid. Use the acid hot and pour it back on the filter until all of the iron hydroxide, which will carry all of the phosphorus, is dissolved off the filter. Wash the filter with some 1 : 40 nitric acid about twenty times or until the washings do not give an appreciable iron test with KCNS. Evaporate the filtrate and washings to 15 c.c. Add 15 c.c. of water, boil with a slight excess of KMnO<sub>4</sub> solution, clear the excess of manganese oxide away with ferrous sulphate, add molybdate to the hot solution and finish as in steel.

Those who are interested in more elaborate details are referred to the preliminary report of the committee already referred to, or to Technical Paper No. 8 of the Department of the Interior, Bureau of Mines, Washington, D. C., Entitled Methods of Analyzing Coal and Coke, by Frederick M. Stanton and Arne C. Fieldner. The authors also give the method they use for the determination of nitrogen in coal. The preliminary report of the Committee on Coal Analysis can be found in Vol. 5, No. 6, of the Journal of Industrial and Eng. Chemistry.



*Coke Analysis.*

*Carbon.* The author determines the total carbon, as in the analysis of graphite, by burning 0.200 gram of the coke in the electric combustion furnace.

*The sulphur* is obtained by fusing 0.5 gram of the coke in an iron crucible with 15 grams of sodium peroxide mixed with 10 grams of sodium carbonate. The fusion is then dissolved out with water and finished as given for sulphur in coal.

*The ash* is obtained as in coal.

## CHAPTER XX.

### PART I.

#### THE PERCENTAGE REDUCTION OF A SUBSTANCE IN SOLUTION TO ANY DESIRED PERCENTAGE.

LET  $P$  = the percentage of the substance in the concentrated solution.

Let  $p$  = the lower and desired percentage of the substance.

Let  $A$  = the specific gravity of the concentrated solution.

Let  $W$  = the amount of water necessary to add to 1 c.c. of the conc. solution to reduce it to the desired lower percentage.

Then

$$W = \left( \frac{P - p}{p} \right) A.$$

#### CALCULATIONS.

Suppose the specific gravity of a given sample of nitric acid is found by means of a hydrometer to be 1.400 at a temperature of 20° C. By table No. 1 we find that the difference in specific gravity for 1° C. between 1.37 sp. gr. and 1.405 is from 0.0013 to 0.0014, or a total difference of 0.0001 for a variation of 0.035 in specific gravity. Now 1.400 is 0.030 above 1.37 in specific gravity, therefore the correction for 1 degree at 1.400 is 0.0013 plus  $\frac{8}{35}$  of 0.0001, or 0.0013 plus 0.000085, or 0.001385. Since the temperature was 20 degrees, then the specific gravity of the given acid if cooled to 15 degrees would be 1.40 plus 0.00138  $\times$  5, or 1.4069. By the table we find that the nearest specific gravity, or 1.405, gives a percentage of 66.40. Further, the percentage correction at this point for 0.001 of specific gravity is 0.220. Therefore, the percentage of the given concentrated acid at 15 degrees would be 66.40 plus 0.220  $\times$  1.9, or 66.4 plus 0.418, or 66.818, or  $P$  in the reduction formula.

For example, if it is desired to reduce this 66.818 per cent acid at 15 degrees to 32 per cent acid at 15 degrees, then we have

$$\frac{66.818 - 32.00}{32.00} \times 1.4069, \text{ or } \frac{34.818}{32} \times 1.4069, \text{ or } 1.088 \times 1.4069,$$

or 1.530, or every c.c. of the acid requires 1.5307 c.c. of water to reduce it to 32 per cent at 15° C. By consulting table No. 2 it will be seen that 1000 c.c. acid of 1.407 specific gravity requires 1531.8 c.c. of water to reduce it to 32 per cent acid at 15° C.

In like manner, if it is required to obtain 20 per cent acid from 66.818 per cent acid:  $\frac{66.818 - 20}{20} \times 1.4069, \text{ or } \frac{46.818}{20} \times 1.4069,$   
or  $2.3409 \times 1.4069$ , or 3.2934. That is, 1 c.c. of 66.818 per cent acid requires 3.2934 c.c. of water to dilute it to 20 per cent acid at 15° C.

#### USE OF TABLE No. 2.

Having by means of table No. 1 calculated the observed specific gravity to 15 degrees, then from table No. 2 the amount of water required to reduce such an acid to 32 per cent or 20 per cent is read either direct or by interpolation.

In a similar way one can reduce concentrated ammonia to any desired lower percentage, the only difference being that in calculating to 15° C. the correction for percentage is subtractive instead of additive as in the case of acids, the reason, of course, being that the greater the density of ammonia solution in water, the lower the percentage of NH<sub>3</sub> therein.

If one needs to prepare from concentrated ammonia an 11.50 per cent solution, first, dilute two parts of the former with one part of water and cool to the room temperature. Let the reading be 0.9385 at 23° C. The correction for 1° C. at 0.938 by table No. 3 is 0.0004 for specific gravity. The total correction for the 8 degrees is 0.0004 × 8, or 0.0032. The specific gravity of the ammonia at 15 degrees is therefore 0.9385 plus 0.0032, or 0.9417. By the table the nearest lower specific gravity is 0.940, which corresponds to 15.63 per cent ammonia. The percentage correction for 0.001 of specific gravity at this point is 0.295.

Therefore, the total correction is  $0.295 \times 1.7$ , or  $0.5015$ . Hence, the percentage for a specific gravity of  $0.9417$  is  $15.63 - 0.5015$ , or  $15.1285$ . To reduce this percentage to  $11.50$  the formula gives the following:

$$\frac{15.128 - 11.50}{11.50} \times 0.9417 \text{ equals } 0.297, \text{ or } 1 \text{ liter of this ammonia}$$

would require 297 c.c. of water to dilute it to  $11.50$  per cent at  $15^{\circ}\text{C}$ .

For further illustration, suppose it is necessary to obtain the percentage of ammonia corresponding to a specific gravity of  $0.947$  at  $22$  degrees. The correction for specific gravity per  $1$  degree of temperature at the nearest point in the table ( $0.946$ ) is  $0.00036$ . As the reading was taken  $7$  degrees above the  $15$  degrees, then the total correction is  $0.00036 \times 7$ , or  $0.00252$ , and the corrected reading is  $0.947$  plus  $0.00252$ , or  $0.9495$ . The nearest lower specific gravity in table No. 3 is  $0.948$ , being equivalent to a percentage of  $13.31$ . Now the correction for percentage at this point is  $0.285$  for every  $0.001$  of specific gravity. The total correction is  $0.285 \times 1.5$ , or  $0.427$ . The percentage of the ammonia for  $0.9495$  at  $15$  degrees is  $13.31 - 0.427$ , or  $12.88$  per cent.

## THE PERCENTAGE REDUCTION OF A SUBSTANCE, ETC. 407

TABLE I.  
AQUEOUS SOLUTIONS OF NITRIC ACID.  
From a Table by Lunge and Rey. Specific Gravities and Percentages HNO<sub>3</sub>.

Specific Gravity $d \frac{15^{\circ}}{4^{\circ}}$ C.	Percent- age HNO <sub>3</sub>	Difference in Specific Gravity for 1° C. between 13° and 17°.	Difference in Percent- age for 0.001 Specific Gravity.	Specific Gravity $d \frac{15^{\circ}}{4^{\circ}}$ C.	Percent- age HNO <sub>3</sub>	Difference in Specific Gravity for 1° C. between 13° and 17°.	Difference in Percent- age for 0.001 Specific Gravity.
I. 055	9.84	0.0003	.....	I. 280	44.41	0.0009	0.154
I. 060	10.68	0.0003	0.168	I. 285	45.18	0.0010	0.154
I. 065	11.51	0.0003	0.166	I. 290	45.95	0.0010	0.154
I. 070	12.33	0.0003	0.164	I. 295	46.72	0.0010	0.154
I. 075	13.15	0.0004	0.164	I. 300	47.49	0.0010	0.154
I. 080	13.95	0.0004	0.160	I. 305	48.26	0.0010	0.154
I. 085	14.74	0.0004	0.158	I. 310	49.07	0.0010	0.162
I. 090	15.53	0.0004	0.158	I. 315	49.89	0.0011	0.164
I. 095	16.32	0.0004	0.158	I. 320	50.71	0.0011	0.164
I. 100	17.11	0.0004	0.158	I. 325	51.53	0.0011	0.164
I. 105	17.89	0.0005	0.156	I. 330	52.37	0.0011	0.168
I. 110	18.67	0.0005	0.156	I. 335	53.22	0.0011	0.170
I. 115	19.45	0.0005	0.156	I. 340	54.07	0.0011	0.170
I. 120	20.23	0.0005	0.156	I. 345	54.93	0.0011	0.172
I. 125	21.00	0.0005	0.154	I. 350	55.79	0.0011	0.172
I. 130	21.77	0.0005	0.154	I. 355	56.66	0.0012	0.174
I. 135	22.54	0.0006	0.154	I. 360	57.57	0.0012	0.182
I. 140	23.31	0.0006	0.154	I. 365	58.48	0.0012	0.182
I. 145	24.08	0.0006	0.154	I. 370	59.39	0.0013	0.182
I. 150	24.84	0.0006	0.152	I. 375	60.30	0.0013	0.182
I. 155	25.60	0.0006	0.152	I. 380	61.27	0.0013	0.194
I. 160	26.36	0.0006	0.152	I. 385	62.24	0.0013	0.194
I. 165	27.12	0.0007	0.152	I. 390	63.23	0.0013	0.198
I. 170	27.88	0.0007	0.152	I. 395	64.25	0.0013	0.204
I. 175	28.63	0.0007	0.150	I. 400	65.30	0.0013	0.210
I. 180	29.38	0.0007	0.150	I. 405	66.40	0.0014	0.220
I. 185	30.13	0.0007	0.150	I. 410	67.50	0.0014	0.220
I. 190	30.88	0.0007	0.150	I. 415	68.63	0.0014	0.226
I. 195	31.62	0.0007	0.150	I. 420	69.80	0.0014	0.234
I. 200	32.36	0.0007	0.148	I. 425	70.98	0.0014	0.236
I. 205	33.09	0.0008	0.146	I. 430	72.17	0.0014	0.238
I. 210	33.82	0.0008	0.146	I. 435	73.39	0.0014	0.244
I. 215	34.55	0.0008	0.146	I. 440	74.68	0.0015	0.258
I. 220	35.28	0.0008	0.146	I. 445	75.98	0.0015	0.260
I. 225	36.03	0.0008	0.150	I. 450	77.28	0.0015	0.260
I. 230	36.78	0.0008	0.150	I. 455	78.60	0.0015	0.264
I. 235	37.53	0.0008	0.150	I. 460	79.98	0.0015	0.276
I. 240	38.29	0.0008	0.152	I. 465	81.42	0.0015	0.288
I. 245	39.05	0.0008	0.152	I. 470	82.90	0.0015	0.296
I. 250	39.82	0.0009	0.154	I. 475	84.45	0.0015	0.310
I. 255	40.58	0.0009	0.152	I. 480	86.05	0.0015	0.320
I. 260	41.34	0.0009	0.152	I. 485	87.70	0.0015	0.330
I. 265	42.10	0.0009	0.152	I. 490	89.60	0.0015	0.420
I. 270	42.87	0.0009	0.154	I. 495	91.60	0.0016	0.400
I. 275	43.64	0.0009	0.154	I. 500	94.09	0.0016	0.498

TABLE 2.  
DILUTION OF CONCENTRATED NITRIC ACID.  
To 20 and 32 Per Cent.

Specific Gravity HNO <sub>3</sub> at 15° C.	Water Added to 1000 c.c.		Variation in Weight, Water for 1° C.	Specific Gravity HNO <sub>3</sub> at 15° C.	Water Added to 1000 c.c.		Variation in Weight, Water, for 1° C.
	20 Per Cent.	32 Per Cent.			20 Per Cent.	32 Per Cent.	
I. 395	3086.4	1405.9	I. 38	I. 433	3790.5	1831.7	I. 88
I. 396	3103.3	1415.8	I. 39	I. 434	3810.6	1843.9	I. 90
I. 397	3120.2	1425.7	I. 40	I. 435	3830.7	1856.1	I. 91
I. 398	3137.1	1435.7	I. 41	I. 436	3852.0	1869.0	I. 92
I. 399	3154.0	1445.6	I. 42	I. 437	3873.3	1881.9	I. 94
I. 400	3171.0	1456.9	I. 43	I. 438	3894.6	1894.8	I. 96
I. 401	3188.7	1467.1	I. 44	I. 439	3915.9	1907.7	I. 98
I. 402	3206.4	1477.4	I. 46	I. 440	3937.0	1920.6	2.00
I. 403	3224.1	1487.6	I. 47	I. 441	3958.5	1933.7	2.02
I. 404	3241.8	1497.9	I. 48	I. 442	3980.0	1946.8	2.03
I. 405	3259.6	1510.4	I. 49	I. 443	4001.5	1959.9	2.05
I. 406	3277.8	1521.1	I. 50	I. 444	4023.0	1973.0	2.06
I. 407	3295.5	1531.8	I. 52	I. 445	4044.6	1986.0	2.07
I. 408	3313.2	1542.5	I. 53	I. 446	4066.2	1999.2	2.09
I. 409	3330.9	1553.2	I. 55	I. 447	4087.8	2012.4	2.10
I. 410	3348.8	1564.2	I. 57	I. 448	4109.4	2025.6	2.11
I. 411	3367.2	1575.3	I. 58	I. 449	4131.0	2038.8	2.12
I. 412	3385.6	1586.4	I. 59	I. 450	4152.8	2051.8	2.13
I. 413	3404.0	1597.5	I. 60	I. 451	4175.1	2065.2	2.15
I. 414	3422.4	1608.6	I. 61	I. 452	4197.4	2078.6	2.17
I. 415	3440.6	1619.7	I. 62	I. 453	4219.7	2092.0	2.19
I. 416	3459.6	1631.2	I. 63	I. 454	4242.0	2105.4	2.21
I. 417	3478.6	1642.7	I. 65	I. 455	4263.2	2118.8	2.22
I. 418	3497.6	1654.2	I. 66	I. 456	4286.3	2132.9	2.24
I. 419	3516.6	1665.7	I. 68	I. 457	4309.4	2147.0	2.25
I. 420	3535.8	1677.4	I. 70	I. 458	4332.5	2161.1	2.26
I. 421	3555.1	1689.1	I. 70	I. 459	4355.6	2175.2	2.27
I. 422	3574.4	1700.8	I. 70	I. 460	4378.5	2189.1	2.28
I. 423	3593.7	1712.5	I. 70	I. 461	4402.6	2203.7	2.30
I. 424	3613.0	1724.2	I. 70	I. 462	4426.7	2218.3	2.32
I. 425	3632.3	1735.8	I. 72	I. 463	4450.8	2232.9	2.34
I. 426	3651.9	1747.6	I. 72	I. 464	4474.9	2247.5	2.36
I. 427	3671.5	1759.4	I. 74	I. 465	4499.0	2262.3	2.38
I. 428	3691.1	1771.2	I. 77	I. 466	4523.8	2277.5	2.41
I. 429	3710.7	1783.0	I. 79	I. 467	4548.6	2292.7	2.44
I. 430	3730.2	1795.1	I. 82	I. 468	4573.4	2307.9	2.47
I. 431	3750.3	1807.3	I. 84	I. 469	4598.2	2323.1	2.50
I. 432	3770.4	1819.5	I. 86	I. 470	4623.2	2338.3	2.55

TABLE 3.  
SPECIFIC GRAVITIES OF AMMONIA SOLUTIONS.

Lunge and Wiernik.

Specific Gravity at 15° C.	Per Cent NH <sub>3</sub> .	Difference in Specific Gravity for 1° C.	Difference in Per Cent for 0.001 Specific Gravity.	Specific Gravity at 15° C.	Per Cent NH <sub>3</sub> .	Difference in Specific Gravity for 1° C.	Difference in Per Cent for 0.001 Specific Gravity.
0.980	4.80	0.00023	.....	0.930	18.64	0.00042	0.305
0.978	5.30	0.00023	0.250	0.928	19.25	0.00043	0.305
0.976	5.80	0.00024	0.250	0.926	19.87	0.00044	0.310
0.974	6.30	0.00024	0.250	0.924	20.49	0.00045	0.310
0.972	6.80	0.00025	0.250	0.922	21.12	0.00046	0.315
0.970	7.31	0.00025	0.255	0.920	21.75	0.00047	0.315
0.968	7.82	0.00026	0.255	0.918	22.39	0.00048	0.320
0.966	8.33	0.00026	0.255	0.916	23.03	0.00049	0.320
0.964	8.84	0.00027	0.255	0.914	23.68	0.00050	0.325
0.962	9.35	0.00028	0.255	0.912	24.33	0.00051	0.325
0.960	9.91	0.00029	0.280	0.910	24.99	0.00052	0.330
0.958	10.47	0.00030	0.280	0.908	25.65	0.00053	0.330
0.956	11.03	0.00031	0.280	0.906	26.31	0.00054	0.330
0.954	11.60	0.00032	0.285	0.904	26.98	0.00055	0.335
0.952	12.17	0.00033	0.285	0.902	27.65	0.00056	0.335
0.950	12.74	0.00034	0.285	0.900	28.33	0.00057	0.340
0.948	13.31	0.00035	0.285	0.898	29.01	0.00058	0.340
0.946	13.88	0.00036	0.285	0.896	29.69	0.00059	0.340
0.944	14.46	0.00037	0.290	0.894	30.37	0.00060	0.340
0.942	15.04	0.00038	0.290	0.892	31.05	0.00060	0.340
0.940	15.63	0.00039	0.295	0.890	31.75	0.00061	0.350
0.938	16.22	0.00040	0.295	0.888	32.50	0.00062	0.375
0.936	16.82	0.00041	0.300	0.886	33.25	0.00063	0.375
0.934	17.42	0.00041	0.300	0.884	34.10	0.00064	0.425
0.932	18.03	0.00042	0.305	0.882	34.95	0.00065	0.425

## CHAPTER XX.

### PART II.

#### PLAN AND VIEWS OF CHEMICAL LABORATORY FOR STEEL WORKS PRACTICE.

THE working drawings show an extension planned by the author, and recently added to the laboratory of the Park Works of the Crucible Steel Co. of America. (Pages 411 and 418.)

Central double tables are located at *D*, *D*, and single side tables at *H*, *F*, *E*, *J*, *I*, and a single center one at *G*, Fig. 29-1. Tables *D*, *D*, and *E* are supplied with gas at 8 oz. pressure, compressed air at about eighty pounds and water as shown. At the small deep stone sinks on the ends of the tables are brass water power pumps. Illustration 15, page 247, gives a view of one of these suction outfits where four chromium-vanadium tests can be filtered through porous alundum thimbles, connected to one pump by means of a glass manifold. The circles represent the large wash bottles that are placed on high pedestals.

View 30 shows these bottles above the tables. No. 31 shows the hoods. The halves of *D*, *D*, Fig. 29-1, facing the center aisle are used for combustion work. There is abundant room for eight outfits, four on each half. View 32 shows four combustion furnaces with trains. The other halves of *D*, *D*, are for general analytical work and serve the hoods *C* and *B*, Fig. 29-1.

PLAN AND VIEWS OF CHEMICAL LABORATORY, ETC. 411

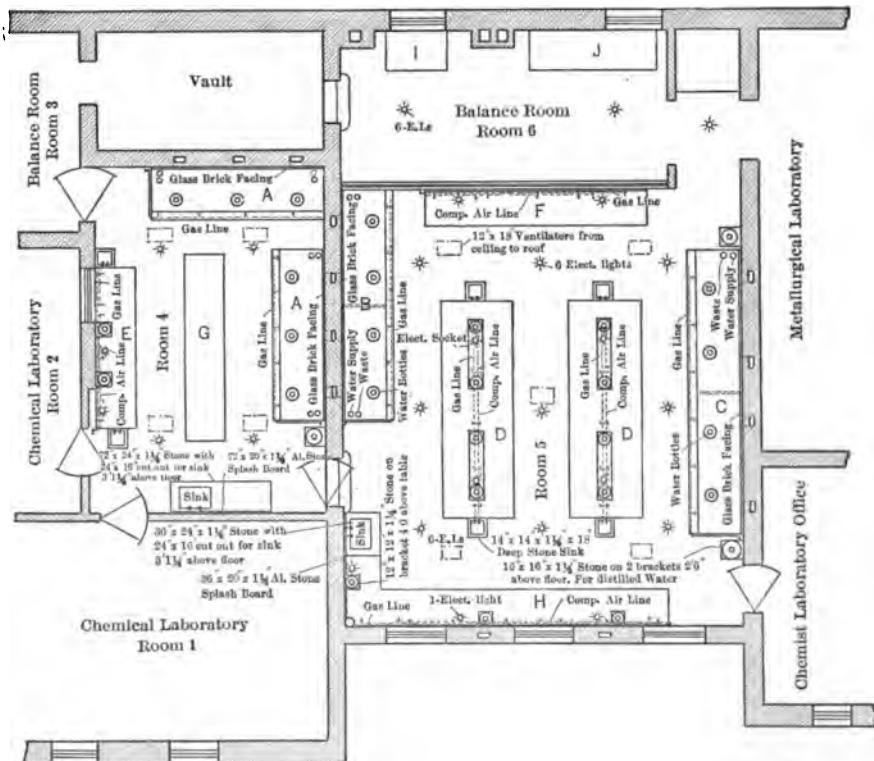


FIG. 29-1.

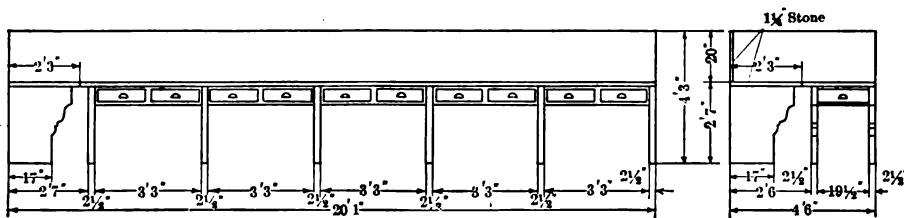
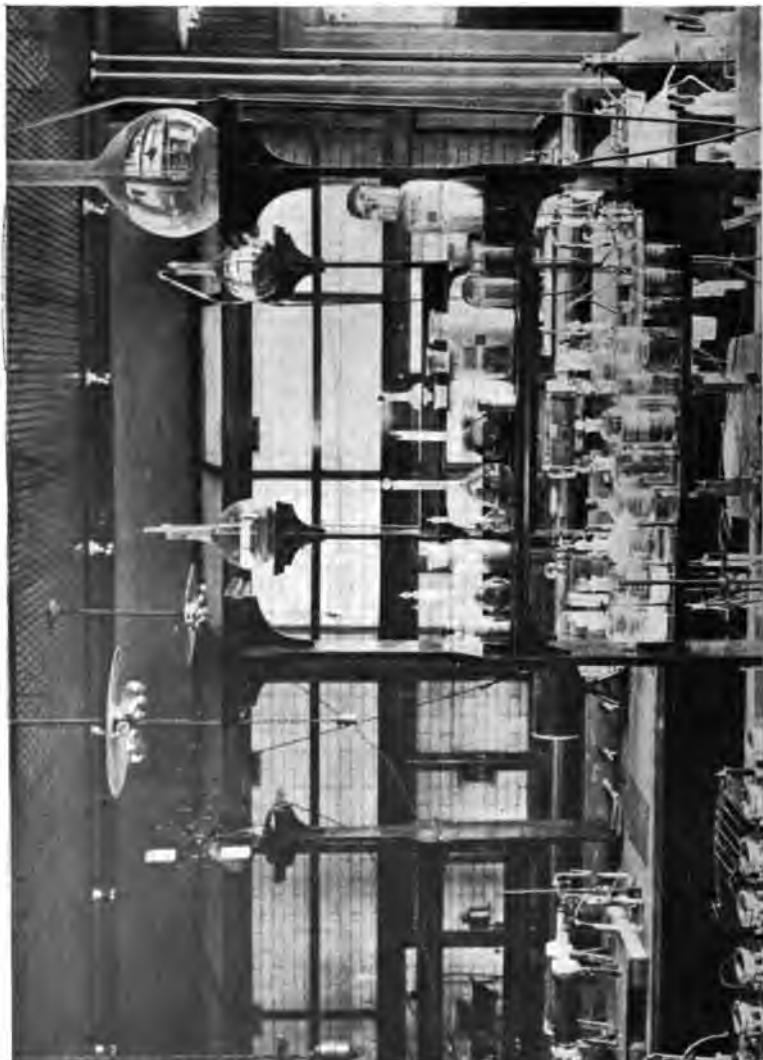


FIG. 29-2.



VIEW 30.



View 3.

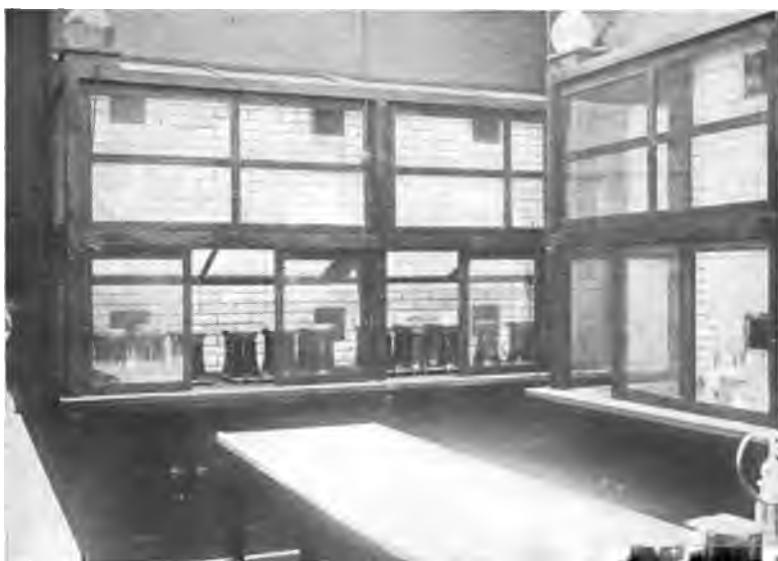


VIEW 32.

PLAN AND VIEWS OF CHEMICAL LABORATORY, ETC. 415



VIEW 33.



VIEW 34.

All hoods are equipped with water and extra heavy lead waste pipes for condensers. View 33 shows one of these brass water cocks of which there are two in each division of the hoods. View

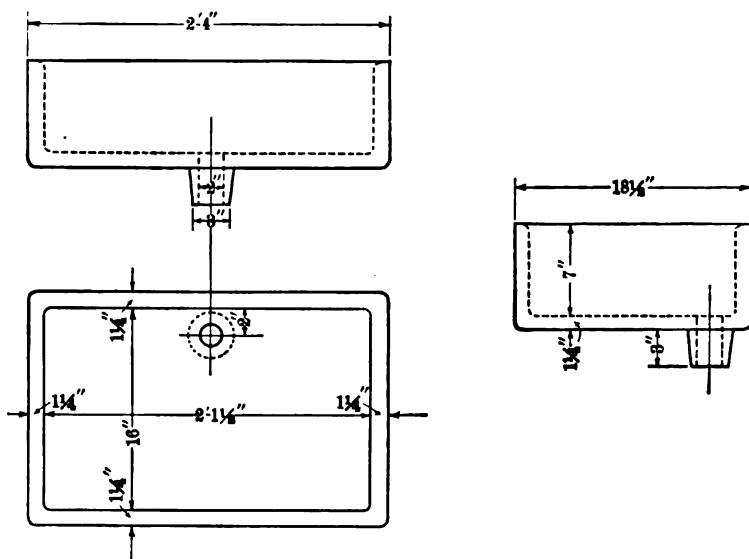


FIG. 35.

33 also shows the way in which the gas is distributed to the various burners from gas cocks concealed in the hood cupboards below. All working surfaces of the hoods and the tables are covered with stone slabs. All heating apparatus is placed on an upper slab set on wooden cross pieces leaving an air space of about  $1\frac{1}{2}$  inches. This removes danger of the stone slabs being cracked by radiated heat. The back walls of hoods are of acid-proof brick with a white surface as shown in Views 31, 33, 34. The latter show the way the hoods are fitted with sliding doors and are framed with cabinet finished straight sawed oak. The sliding doors the author has found to be far superior to any others. The hoods along the walls of the laboratory are much to be preferred to center hoods. The latter cut off the light, do not have a good draught and cannot be backed with acid-proof material. Again the center hood is peculiarly subject to dirt

dropping from its upper parts and its flues. If bits of mortar drop from flues, slanting sash can be set up as shown in the hood at the rear of View 34. These frames are supported on iron rods and can be removed in a few moments when it is desired to clean out the hoods. All tables, hoods and exposed floor lines have stone baseboards to prevent the marring of the woodwork when the floors are mopped or scrubbed. The large sinks near the doorways are made of heavy acid-proof stoneware. The nipple at the outlet of the sink fits into a terra-cotta sewer via a trap of the same material. All joints are caulked with oakum and on top of the latter is poured hot asphaltum. The sinks of this description are practically indestructible. Fig. 35 gives the author's design and dimensions of this acid and alkali proof sink. The sewer from such a sink should never lead away from it in a horizontal direction. The terra-cotta sewer from any sink into which acid, alkali or any corrosive waste is poured should drop vertically to the basement to prevent stoppages and leaks. To prevent broken glass and other odds and ends from getting from the sink into the sewer, a false bottom of oak, perforated with  $\frac{1}{4}$  inch holes should be provided. To prevent the pitch from running out of the joints, in hot weather, it is safer to finish off the joints with a final layer of cement plastered firmly on top of the pitch; it is absolutely necessary to do this when it is impossible to avoid placing a length or two of pipe horizontally.

The elevation of the balance table used in room 5 is shown in the drawing at *H - 1*, Fig. 29-2, page 411. The elevations of the hoods and tables in rooms Nos. 4, 5 and 6 are given at *A - 1*, *B - 1*, *C - 1*, *D - 1*, *E - 1*, *F - 1*, *G - 1*, *I - 1* and *J - 1*, respectively (see Figs. 29-2-3).

The stone tops of all of the work tables are covered with sheet rubber packing of about one-eighth inch thickness. This material makes a nice appearance and prevents considerable breakage of glassware.

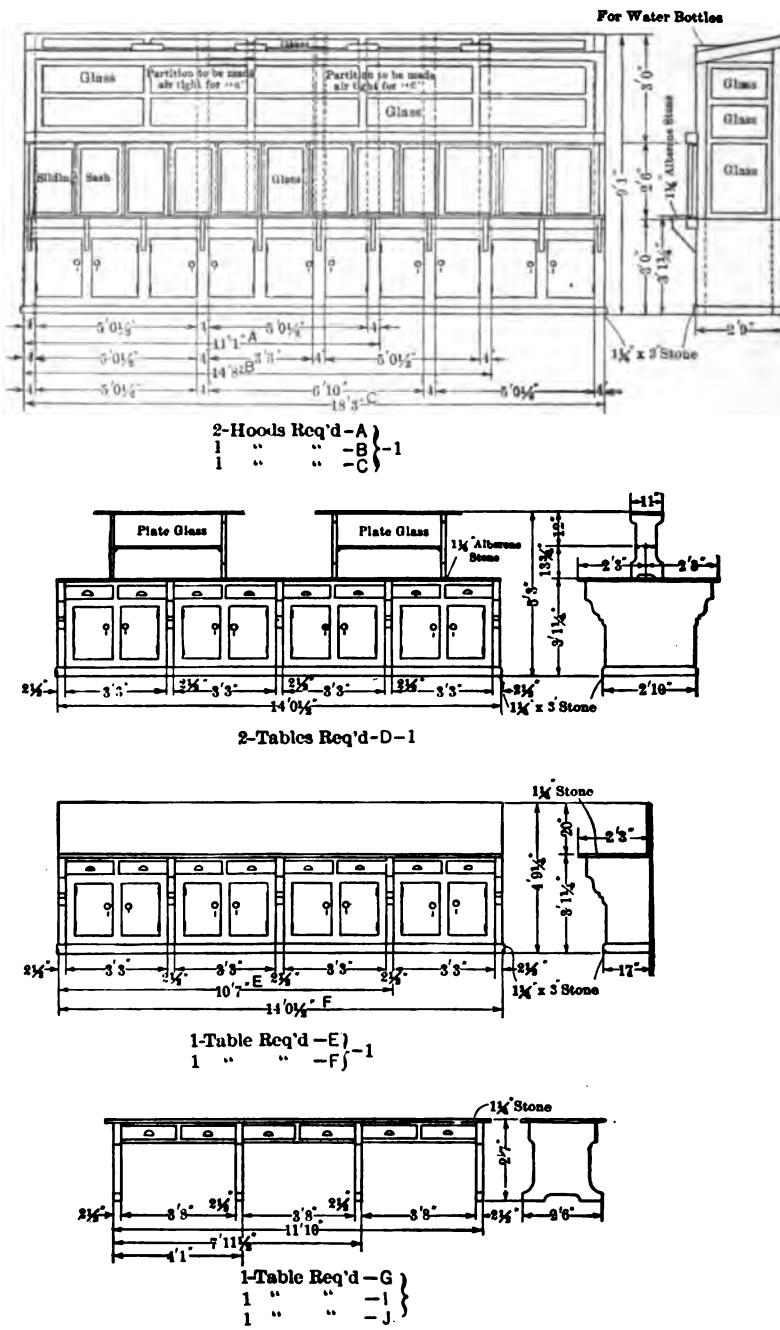


FIG. 29-3.

## CHAPTER XX.

### PART III.

#### THE MAKING AND REPAIRING OF LABORATORY ELECTRIC FURNACES.

IT is quite an economy and instructive for the chemist to build and repair his own electric muffle and combustion furnaces.\* The modern laboratory cannot afford to be without such equipment. The author uses a true ni-chrome wire of German manufacture. For the carbon combustion furnaces, No. 20 gauge wire, 0.032 diameter, is a convenient size. Its resistance is 0.537 ohm per foot. With a voltage ranging as high as 240, direct current, 90 feet of this size is about right and gives a service of three or more months, running 24 hours per day. The wire is coiled around a  $\frac{3}{16}$  diameter rod held in guides and run by a  $\frac{1}{2}$  horse power motor. The cost of a rewiring is as follows:

Wire.....	\$1.00
Labor.....	0.75
Clay core.....	1.25
Incidentals.....	0.25
Total	\$3.25

The expressage is saved to and from the professional repairman and the delay of waiting for the return of the apparatus is avoided.

The coiled wire is wrapped spirally around the clay core, taking precaution that the turns of the spiral do not touch each other as they wind around the core. The ends of the coil are secured at each end of the core with asbestos cord, being tied to the latter. The turns of the wire are then covered with a blanket of alundum cement. The core is put in a warm place until dry. At each end of the coil two or three inches of the wire are left

\* The author ventilates his electric muffle furnaces when igniting filter papers, etc., by blowing a regulated stream of air through the furnace.

uncoiled for connection with the power. One of the cores with the wire on it is shown in Fig. 13, page 242. The cement is plastered over the spiral of wire, shown in the figure. The chemist can readily follow these details by taking such a furnace apart.\*

A large muffle furnace can be built by any laboratory. A sheet iron frame can be used for the sides. The top and bottom of the shell can be in the form of lids of the same material. It is well to place at the top and bottom of each corner of the frame, and on the inside of it, right angle strips of hoop iron. These make the shell more rigid. The opening for the muffle should be central and the frame or shell should be just as deep as the muffle is long, so that the muffle will rest in the frame and come just flush with the outside of the shell. The muffle opening in the frame should fit exactly around the outside of the ends of the muffle, so that very little plastering around it with the cement will be necessary. The writer uses No. 17 gauge wire for the muffle furnaces, that is, 0.045 inch diameter. Three coils are wound around the muffle and connected in parallel. The writer places the parallel leads on the *outside* of the furnace shell, thereby keeping the leads away from the heat, and more accessible. The leads are enclosed in red fiber insulating tubes and supported in brass brackets. One lead is placed on the right side of the furnace shell and the other on the left side. This gives a neat appearance. Where the ends of the coils pass through the metal shell, they are carried through small quartz or pipe clay insulating tubes to join the leads. Each coil is 120 feet long for a 240 volt, direct current. The heat is regulated by means of a theater dimmer of 14 to 25 amps. capacity. The doors are sheet iron, lined with fire brick. They slide up and down† in sheet iron guides and are hung on a

\* The author is now trying the plan of wiring directly on his tapered clay combustion tube. This gives a combustion furnace that will come to full heat in 30 minutes, and saves the cost of the core tube.

† Or the door can be made to open on side hinges, horizontally. Such a door can be lined with a fire brick that fits the muffle opening and projects into the same. This liner keeps heat in better than one that slides up and down. The author finds it convenient to mold and burn his own liners.

lever. The leads are of No. 8 gauge ni-chrome wire of the same make as the heating wire. The furnace shell is given a coat of stovepipe enamel and, if preferred, it can be then given a white finish consisting of two coats of aluminum paint. The wire for such a furnace will cost \$3.00; the clay muffle of composite clay is the most durable and can be had for \$3.50. To this should be added one day's time for the tinner to cut out the shell and the cost of the sheet iron, some rivets, bolts, nuts, metal washers, fifty pounds of magnesia oxide to fill in all spaces around the core and retain the heat. The entire inside

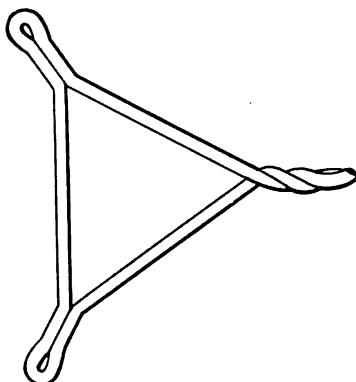


FIG. 36.

of the shell except the space occupied by the muffle is filled with this non-conducting powder. Four right angle strips of sheet brass about  $\frac{1}{8}$  inch thick will be needed to support the leads. The whole cost is a mere trifle compared to the price one must pay for such a furnace made to order. The muffle is rectangular; it is  $8\frac{1}{4}$  inches  $\times$   $6\frac{1}{2}$  inches  $\times$  14 inches. The furnace shell is 14 inches deep to fit the length of the muffle. It is  $16\frac{1}{2}$  inches wide and 15 inches high. To hold such a furnace at any desired temperature from  $200^{\circ}\text{C}.$  to  $1000^{\circ}\text{C}.$  the current should be controlled with a dimmer or rheostat of from at least 12 to 2.5 amperes and a resistance of not less than 60 ohms.

**THE NI-CHROME ONE PIECE TRIANGLE.**

Fig. 36 shows a one piece triangle designed by the author which any one can make in a few minutes from the well annealed German ni-chrome wire. It is practically indestructible. The one shown was made from No. 8 gauge wire.

**SANITARY LABORATORY WASH BOTTLE.**

Fig. 37 shows a wash bottle that is much used in this laboratory for washing precipitates. It has the advantage that the lips do not touch it. It is operated by a slight push of the thumb on the rubber bulb *A*. The little tube at *P* enables

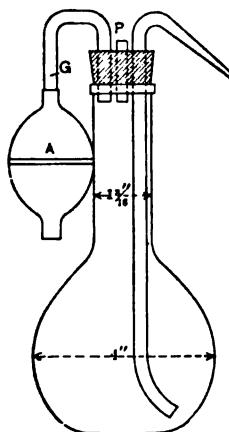


FIG. 37.

the operator to instantly relieve pressure when a washing is finished, avoiding spattering of the washing fluid and excessive amounts of the wash per application.

The rubber bulb is attached to the glass tube *G*. The capacity of the flask is 500 c.c. It has a fire finished ring neck and takes a No. 6 rubber stopper.

## CHAPTER XXI.

### PART I.

#### AN AUTOMATIC STEAM WATER STILL.

AFTER submitting to considerable annoyance from several types of water stills, the author decided to try steam coils as a source of heat.

The boiling of water by this means is not a new idea, but after more than a year's trial, there was finally evolved a form of still which has proven so satisfactory and the flow of the water has been so abundant that the details of the apparatus may be of assistance to someone else.

Two of these stills are in use in our laboratory operating but part of each day. The supply is ample for all analytical needs and for drinking water, which is also furnished to a large office force.

Cold water from the tap enters the condenser jacket *C*, Fig. 38, through the cock *A*. The condenser jacket is a cylindrical copper vessel 11 inches in diameter and 15 inches high. The cooling water overflows at *B* to a sink not shown. A glass\* tube siphon *S'*, *S''*, *S'''*, dipping into the water slightly below the level of *B*, carries hot water continually to the heating chamber *D* by way of the large copper feed funnel *F'*, *F''*.

When the water in *D* has risen several inches the steam is turned into the worm coils of *D* at the valve *V*. These coils consist of two 12-foot lengths of  $\frac{3}{4}$  inch bore copper pipe,† brazed together and coiled around the inside walls of *D*. The steam from the boiling water rises into the dome and passes

\* A brass tube is now used as it is more durable.

† The outside diameter of the copper pipe is one and one-sixteenth inches and the wall is one-eighth inch.

off through a block tin condensing pipe of  $\frac{1}{8}$  inch\* inside diameter at *T* and travels through this pipe, which is coiled in a worm as shown in *C*.

The tin pipe passes through the tubular outlet *O'*, *O''* and delivers the distilled water on a filter paper supported by a six

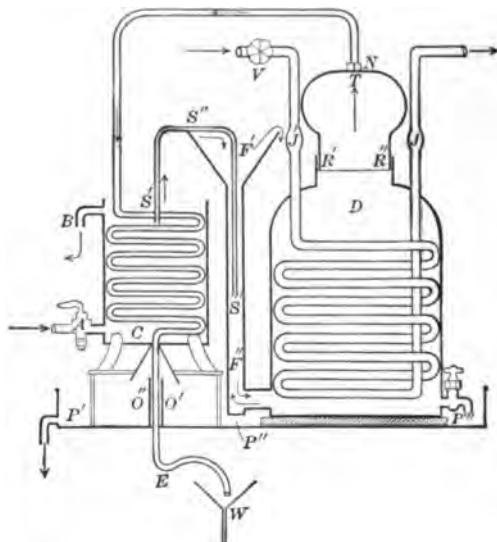


FIG. 38.

inch ribbed glass funnel *W*. The filter papers are 30 cm. and are folded to fit the funnel. A piece of cheese-cloth is folded in the apex of the filter paper cone to prevent the weight of the water from breaking the paper. The filter paper catches any oily matter or other particles carried over with the steam.

The distillate is delivered to the receiving funnel at the rate of one liter every 3 minutes when sufficient pressure is main-

\* The larger the inside diameter of the tin worm the better to secure rapid condensation and a large output of water.

The block tin worm now in use is  $\frac{1}{8}$  to 1 inch O. D.;  $\frac{1}{8}$  to  $\frac{1}{2}$  wall; and  $\frac{1}{8}$  bore. The regular commercial sizes approximating these dimensions are used. A number of these stills are now in use.

tained in *D* to keep the copper funnel *F'*, *F''* filled nearly to overflowing with hot water.

The water reservoir is a nine gallon bottle, in the neck of which the funnel *W* rests. The bottle, which is not shown, is inclosed in a cupboard in which is an electric light to dispel darkness and roaches. This bottle rests in a copper pan, which is drained to the sewer. The tin pipe is bent into an elbow at *E* so that any condensation of moisture on damp days drips off at *E* instead of running down the pipe into *W*.

Steam pressure furnished from the mills is liable to continual variation. The amount of pressure may be nicely adjusted at *V*, but subsequent increase of pressure often causes the water to boil over at *F* and splash down into the copper pan *P'*, *P''*, *P'''*, which is drained at *P'*. The pan is five inches deep and large enough to contain the entire apparatus.

To clean the still the tin pipe is unscrewed at *N*, the dome head is removed, and water is played on the interior of *D* with a hose, washing the sediment out through the cock at *P'''*.

The steam dome rests in the neck of *D* and is calked steam tight with cheese-cloth. The cloth is stretched in a diaphragm across *R'*, *R''*, with enough excess of cloth for calking purposes.

The boiling of the water in *F'*, *F''* in no way prevents the action of the siphon *S'*, *S''*, *S'''*. The heating coils of *D* are joined to ordinary steam pipes of the same diameter at *J'*, *J''*.

This still could be made in any size to suit a greater or less production than that mentioned, a smaller size for a household or small laboratory, and in larger sizes for office buildings or for manufacturers needing a large supply of distilled water. A number of these stills are now in use.

## CHAPTER XXI.

### PART II.

#### CLAY COMBUSTION BOATS.

THE clay boats are made from Klingenberg clay.\* A typical analysis of it is given herewith:

	Per cent.
Protoxide of iron.....	2.67
Silica.....	52.48
Alumina.....	29.46
Ignition loss.....	14.18

Any plastic clay free from grit would answer just as well. The clay is ground to pass a 30-mesh sieve, and is thoroughly kneaded to a stiff dough with water. It is then rolled in a towel. By wetting the towel occasionally, the clay can be kept ready to use as long as desired.

The clay is rolled on a moist plaster-of-paris slab into a cigar shape and pressed into the plaster-of-paris mold with the thumbs. The excess clay is scraped off with a thin-edged piece of wood. The guide strip is then laid on the mold. It is the exact duplicate of the face of the mold, or *pmno* as shown in the plan. This strip, of course, has an opening in it coinciding exactly with *IcdJ*, Fig. 39. The strip can be fastened on by a gum band at each end. The wooden tool *T* is plunged down through this slot, and, while being held perfectly vertical, it is slid along the wooden guide strip, scooping out the clay and shaping the interior of the boat. The tool slides along the strip on its surfaces at *R* and *R'*. The distances from *c'* to *R* and from *R'* to *d'* are equal and conform to the thickness of the guide strip. The distance *c'd'* equals *cd*. *c'V* and *V'd'* regulate the thickness of the walls of the boat. *Vf'V'* forms the interior of the boat. The tool *T* is rounded on one side and is trimmed to a thin edge on the rounded

\* A blend of clays gives better results.

side. The tools are kept in water, when not in the operator's hand, to prevent the clay from sticking to them. The interior of the mold has a flat bottom. The author prefers a boat of the following outside dimensions when burned: 15 mm. wide at

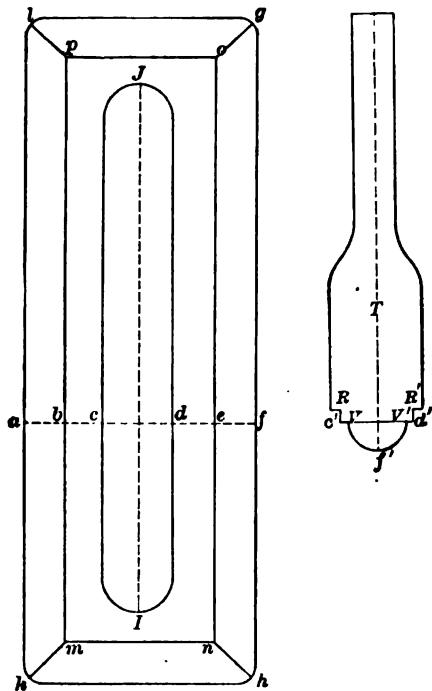


FIG. 39.

top by 7 mm. wide at bottom by 9 mm. high by  $13\frac{1}{2}$  mm. long. The bowl of the mold should be about 6 per cent larger in all its dimensions to allow for shrinkage.

After the interior has been properly shaped, the guide strip is removed, the face of the mold scraped clean, and the mold put away in a warm place for the clay to dry. Slow drying for one or two days is the best. When the boats no longer seem damp to the touch, they are removed from the molds and dried for several hours in an air bath at a temperature of  $120^{\circ}\text{C}$ . They are then put in a muffle furnace, and the latter is lighted and

the heat brought as quickly as convenient to a temperature of  $850^{\circ}$  to  $900^{\circ}$  C. (very bright red-heat) and kept at that temperature for from two to four hours. The heat is then turned off and the boats are ready for use. A boy can easily mold forty boats in three hours, and, after the molding is completed, the remaining operations require but a few moments' attention to make the transfers from the drying space to the air bath, and from the latter to the muffle furnace.

The boat should have walls and bottoms about  $\frac{1}{8}$  inch thick. Boats made as described answer all of the purposes of porcelain boats, and, one can readily see, are extremely cheap. The writer first experimented with a view to making his own boats, more than 4 years ago, and now uses them for all combustion work.

It is convenient to have the dimension  $Kh$ , 62 mm.;  $hg$ , 177 mm., and the total thickness of the mold 25 mm.

When the boats have been burned, two or three from each batch should be placed in the combustion furnace and a blank analysis made. If the weighing apparatus shows a gain of more than 0.0002 gram, it is an indication of imperfect burning of the boats. They should be reburned until free from all carbonaceous matter.

The author wishes to acknowledge the assistance and advice rendered him by the superintendent of the plumbago crucible factory of this works, Mr. Bayard Guthrie, in working out the method of making a cheap substitute for porcelain combustion boats.

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